Reports of the Finnish Environment Institute 38 | 2021

Interlaboratory Proficiency Test 05/2021

Natural and drinking water metal analyses

Mirja Leivuori, Riitta Koivikko, Timo Sara-Aho,
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FINAS
Finnish Accreditation Service
PT01 (EN ISO/IEC 17043)

Reports of the Finnish Environment Institute 38 | 2021
Finnish Environment Institute
Laboratory Centre

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Publisher and financier of publication: Finnish Environment Institute SYKE
Latokartanonkaari 11, 00790 Helsinki, Finland, Phone +358 295 251 000, syke.fi

Layout: Markku Ilmakunnas
Cover photo: Adobe Stock

The publication is available in the internet (pdf): syke.fi/publications | helda.helsinki.fi/syke

ISBN 978-952-11-5426-3 (PDF)
ISSN 1796-1726 (online)

Year of issue: 2021

Abstract

Interlaboratory Proficiency Test 05/2021
Proftest SYKE carried out the proficiency test (PT) for analysis of metals in natural and drinking waters in April-May 2021. The measurands for synthetic sample and drinking as well as natural water samples were: Al, As, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Mg, Mn, Mo, Na, Ni, Pb, Sb, Se, Ti, V, and Zn. In total, there were 15 participants in the PT. Either metrologically traceable concentration, the calculated concentration or the mean or the median of the results reported by the participants was used as the assigned value for the measurands. The overall performance of the participants was evaluated by using z and E_n scores. In this PT 90 % of the results were satisfactory when total deviation of 10–20 % for the measurands was accepted from the assigned value. The titanium results of the drinking water sample D2M were evaluated by using E_n scores and 80 % of those were satisfactory. Warm thanks to all participants in this proficiency test!

Keywords: water analysis, metals, Al, As, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Mg, Mn, Mo, Na, Ni, Pb, Sb, Se, Ti, V, Zn, water, environmental laboratories, proficiency test, interlaboratory comparisons

Tiivistelmä

Laboratorioiden välinen pätevyyskoe 05/2021
Proftest SYKE järjesti pätevyyskokeen metallimäärityksiä tekeville laboratorioille huhti-toukokuussa 2021. Pätevyyskokeessa määritettiin synteettisestä näytteestä sekä talous- ja luonnonvesinäytteistä testisuureet Al, As, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Mg, Mn, Mo, Na, Ni, Pb, Sb, Se, Ti, V ja Zn. Pätevyyskokeeseen oli yhteensä 15 osallistujaa. Testisuureiden vertailuarvoina käytettiin joko metrologisesti jäljitettävää pitoisuutta, laskennallista pitoisuutta tai osallistujien ilmoittamien tulosten keskiarvoa tai mediaania. Osallistujien pätevyyden arviointi tehtiin z- ja E_n-arvojen avulla. Koko tulosaineistossa oli z-arvoilla arvioituna 90 % hyväksyttäviä tuloksia, kun vertailuarvosta sallittiin 10–20 %:n poikkeama. Talousvesinäytteen D2M titaanin tulokset arvioitiin käyttäen E_n-arvoja ja näistä 80 % oli hyväksyttäviä. Kiitos pätevyyskokeen osallistujille!

Asiasanat: vesianalyysi, metallit Al, As, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Mg, Mn, Mo, Na, Ni, Pb, Sb, Se, Ti, V, Zn, vesi- ja ympäristölaboratoriot, pätevyyskoe, laboratorioiden välinen vertailumittaus

Sammandrag

Provningsjämförelse 05/2021
Under april-maj 2021 genomförde Proftest SYKE en provningsjämförelse, som omfattade bestämningen av Al, As, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Mg, Mn, Mo, Na, Ni, Pb, Sb, Se, Ti, V och Zn i syntetisk provet och natur- och hushållsvattenproverna. Denna jämförelse hade totalt 15 deltagarna. Som referensvärde av analytens koncentration användes antingen det metrologiska spårbara värdet, beräknad värdet eller medelvärdet eller median av deltagarnas resultat. Resultaten värderades med hjälp av z- och E_n-värden. I denna jämförelse var 90 % av resultaten värderades med z-värden acceptabla. Resultatet var acceptabel, om det deviera 10–20 % från referensvärdet. Resultaten för titan i hushållsvatten D2M bedömdes med E_n-värden och 80 % var acceptabla. Ett varmt tack till alla deltagarna i testet!

Nyckelord: vattenanalyser, metaller, Al, As, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Mg, Mn, Mo, Na, Ni, Pb, Sb, Se, Ti, V, Zn, provningsjämförelse, vatten- och miljölaboratorier

Contents

1 Introduction 7

2 Organizing the proficiency test 7

2.1 Responsibilities 7

2.2 Participants 8

2.3 Samples and delivery 8

2.4 Homogeneity and stability studies 8

2.5 Feedback from the proficiency test 9

2.6 Processing the data 9

2.6.1 Pretesting the data 9

2.6.2 Assigned values 9

2.6.3 Proficiency assessment procedure 10

3 Results and conclusions 10

3.1 Results 10

3.2 Analytical methods 12

3.3 Uncertainties of the results 13

4 Evaluation of the results 15

5 Summary 17

6 Summary in Finnish 17

References 18

Appendix 1. Participants in the proficiency test 19

Appendix 2. Sample preparation 20

Appendix 3. Homogeneity of the samples 22

Appendix 4. Feedback from the proficiency test 23

Appendix 5. Evaluation of the assigned values and their uncertainties 24

Appendix 6. Terms in the results tables 26

Appendix 7. Results of each participant 27

Appendix 8. Summaries of the z and E_n scores 45

Appendix 9. z scores in ascending order 47

Appendix 10. Results grouped according to the methods 70

Appendix 11. Examples of measurement uncertainties reported by the participants 94

1 Introduction

Proftest SYKE carried out the proficiency test (PT) for analysis of metals in natural and drinking waters in April-May 2021 (MET 05/2021). The measurands for the synthetic sample and drinking as well as natural water samples were: Al, As, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Mg, Mn, Mo, Na, Ni, Pb, Sb, Se, Ti, V, and Zn. In the PT the results of Finnish participants providing environmental data for Finnish environmental authorities were evaluated. Additionally, other water and environmental laboratories were welcomed in the proficiency test.

Finnish Environment Institute (SYKE) is appointed National Reference Laboratory in the environmental sector in Finland. The duties of the reference laboratory include providing interlaboratory proficiency tests and other comparisons for analytical laboratories and other producers of environmental information. This proficiency test has been carried out under the scope of the SYKE reference laboratory and it provides an external quality evaluation between laboratory results, and mutual comparability of analytical reliability. The proficiency test was carried out in accordance with the international standard ISO/IEC 17043 [1] and applying ISO 13528 [2] and IUPAC Technical report [3]. Proftest SYKE is accredited by the Finnish Accreditation Service as a proficiency testing provider (PT01, ISO/IEC 17043, www.finas.fi/sites/en). The organizing of this proficiency test is included in the accreditation scope of Proftest SYKE.

2 Organizing the proficiency test

2.1 Responsibilities

Organizer
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The responsibilities in organizing the proficiency test

Mirja Leivuori	coordinator
Riitta Koivikko	substitute for coordinator
Keijo Tervonen	technical assistance
Markku Ilmakunnas	technical assistance
Sari Lanteri	technical assistance
Ritva Väisänen	technical assistance
Analytical expert	Teemu Näykki, SYKE, Hg, ID-ICP-MS
	Timo Sara-Aho, SYKE, other measurands, ID-ICP-MS
Expert laboratory	SYKE, Helsinki (T003, www.finas.fi/sites/en)

2.2 Participants

In total 15 laboratories participated in this PT, 13 from Finland and 2 from abroad (Appendix 1). 93 % of the participants reported that they have accredited quality management system based on ISO/IEC 17025. Almost 73 % of the participant used accredited analytical methods at least for a part of the measurements. For this PT, the expert laboratory has code 2 in the result tables.

2.3 Samples and delivery

Three types of samples were delivered to the participants: synthetic sample and natural (lake water) as well as drinking water samples.

When preparing the samples, the purity of the used sample vessels was controlled. The randomly chosen sample vessels were filled with deionized water and the purity of the sample vessels was controlled after three days by analyzing Cd, Cu, Hg, and Zn. According to the test results all used vessels fulfilled the purity requirements.

The synthetic sample A1M was prepared from the NIST traceable commercial reference material produced by Inorganic Ventures. The synthetic sample A1Hg was prepared by diluting from the NIST traceable AccuTrace™ Reference Standard produced by AccuStandard, Inc. The sample D2M was domestic water of Helsinki. The sample N3M was lake water collected from the Lake Bodomjärvi, located in southern Finland. To these samples additions of single element standard solutions (Merck CertiPUR®) were done when needed (Appendix 2). The water samples were acidified with nitric acid with the exception of samples for mercury, which were acidified with the hydrochloric acid.

The samples were delivered on 19 April 2021 to the participants abroad and to the national participants on 20 April 2021. The samples arrived to the participants on 21 April 2021.

The samples were requested to be measured as follows:

- Hg samples at the latest on 30 April 2021
- Other samples at the latest on 7 May 2021

The results were to be reported at the latest on 7 May 2021. The majority of the participants delivered the results accordingly. One participant delivered their results on 10 May 2021. Therefore, those results are in this report, but they are not included in the statistical processing of the data and the results are not evaluated. The participant can evaluate their performance, and more information is available from the Guide for participant [4]. The preliminary result report was delivered to the participants via ProftestWEB and email on 18 May 2021.

2.4 Homogeneity and stability studies

The homogeneity of the samples was tested by analyzing Cd, Cr, Hg, Pb, Se, and Zn. More detailed information of the homogeneity studies is shown in Appendix 3. According to the homogeneity test results, all samples were considered homogenous. The synthetic samples were prepared from traceable certified reference materials. However, homogeneity of these was confirmed by parallel measurements of two samples.

Based on the earlier similar proficiency tests the water samples are known to be stable over the given time period for the test.

2.5 Feedback from the proficiency test

The feedback from the proficiency test is shown in Appendix 4. The comments from the participants mainly dealt with the sample delivery and their results reporting. The comment from the provider focused to participants' result reporting. All the feedback from the proficiency test is valuable and is exploited when improving the activities.

2.6 Processing the data

2.6.1 Pretesting the data

To test the normality of the data the Kolmogorov-Smirnov test was applied. The outliers were rejected according to the Grubbs or the Hampel test before calculating the mean. The results which differed from the data more than $5 \times s_{rob}$ or 50 % from the robust mean, were rejected before the statistical results handling. If the result has been reported as below detection limit, it has not been included in the statistical calculations.

More information about the statistical handling of the data is available from the Guide for participant [4].

2.6.2 Assigned values

For the synthetic sample A1M the NIST traceable calculated values were used as the assigned values, with the exception of Hg and Pb. The assigned values for Hg and Pb are based on the results of the metrologically traceable isotope dilution (ID) ICP-MS technique for the samples A1M, A1Hg, D2M, D2Hg, N3M, and N3Hg. The assigned value based on the ID-ICP-MS method is the mean of the homogeneity results and the test result (9 or 12 results). The ID-ICP-MS method is accredited for soluble lead and mercury in synthetic sample, natural and waste waters in the scope of SYKE calibration laboratory (K054; www.finas.fi/sites/en). For the other samples and measurands the mean or the median of the reported results was used as the assigned value due to the number of results was low (n_{stat} <12, Appendix 5). **After reporting the preliminary results no changes have been done for the assigned values.**

The mean or the median of the participant results is not metrologically traceable assigned value. As it was not possible to have metrologically traceable assigned value, the mean or the median of the reported results was the best available value to be used as the assigned value. The reliability of the assigned value was statistically tested [2, 3].

For the calculated assigned values, the expanded uncertainty (k=2) was estimated using standard uncertainties associated with individual operations involved in the preparation of the sample. The main individual source of the uncertainty was the uncertainty of the concentration in the stock solution.

When the mean or the median of the participant results was used as the assigned value, the uncertainty was calculated using the robust standard deviation or the standard deviation, respectively [2, 4]. For the metrologically traceable mercury and lead results, the uncertainty is the expanded measurement uncertainty of the ID-ICP-MS method.

The uncertainties of the calculated and the metrologically traceable assigned values for metals in the synthetic samples varied between 0.4 and 3 %. When using the mean or the median of the participant results as the assigned value, the uncertainties of the assigned values varied between 0.8 and 9.7 % (Appendix 5).

2.6.3 Proficiency assessment procedure

The results of this proficiency test were evaluated both with the z and E_n scores.

The standard deviation for proficiency assessment was estimated based on the measurand concentration, the results of homogeneity and stability tests, the uncertainty of the assigned value, and the long-term variation in the former proficiency tests. The standard deviation for proficiency assessment ($2\times s_{pt}$, at the 95 % confidence level) was set to 10–20 % depending on the measurement.

After reporting the preliminary results no changes have been done for the standard deviations of the proficiency assessment values.

When the number of reported results was low (Ti in the sample D2M, $n_{stat}<6$), the assigned value based on the participants' results and the uncertainty was set for the assigned value, the performance was estimated by means of E_n scores ('*Error, normalized*', Appendix 6).

When using the mean or the median as the assigned value, the reliability was tested according to the criterion $u_{pt} / s_{pt} \leq 0.3$, where u_{pt} is the standard uncertainty of the assigned value and s_{pt} is the standard deviation for proficiency assessment [2, 3]. When testing the reliability of the assigned value the criterion was mainly fulfilled and the assigned values were considered reliable.

The reliability of the standard deviation for proficiency assessment (s_{pt}) and the corresponding z score was estimated by comparing (s_{pt}) with the standard deviation (s, $n_{stat}<12$) of the reported results (the criterion) [3]. The uniformity criterion s_{rob} (or s) / $s_{pt} \leq 1.2$ was mainly fulfilled.

3 Results and conclusions

3.1 Results

The summary of the results is presented in Table 1. The terms in the results table are explained in Appendix 6. The results and the performance of each participant are presented in Appendix 7. The summaries of the z and E_n scores are shown in Appendix 8 and z scores in the ascending order in Appendix 9. The reported results with their expanded uncertainties (k=2) grouped according to the methods are presented in Appendix 10.

The standard deviations of the results varied mainly from 1.1 % to 20 % (Table 1). The standard deviation of results was lower than 10 % for 91 % of the results (Table 1). The highest standard deviation (20.2 %) was for Hg in the synthetic A1Hg sample (Table 1). The robust standard deviations for water samples (Table 1) were approximately on the same level than in the previous similar proficiency test MET 05/2020 [5], where the robust standard deviations varied from 2.1 % to 24 % for the water samples.

Table 1. The summary of the results in the proficiency test MET 05/2021.

Measurand	Sample	Unit	Assigned value	Mean	Rob. mean	Median	s_{rob}	s_{rob} %	s	s %	2 x s_{pt} %	n_{all}	Acc z % / E_n %
Al	A1M	µg/l	25.5	28.2	28.2	28.2	3.0	10.8	2.0	7.2	20	13	75
	D2M	µg/l	14.7	14.8	14.9	14.7	1.8	12.1	1.7	11.3	20	12	91
	N3M	µg/l	527	515	521	527	45	8.6	52	10.2	20	13	83
As	A1M	µg/l	2.25	2.11	2.11	2.14	0.13	6.2	0.11	5.4	15	10	100
	D2M	µg/l	2.16	2.17	2.17	2.16	0.13	5.8	0.11	5.1	10	10	100
	N3M	µg/l	0.64	0.62	0.63	0.64	0.03	4.8	0.03	4.7	10	10	78
B	A1M	µg/l	25.5	26.5	26.5	26.9	2.2	8.3	1.9	7.3	15	11	100
	D2M	µg/l	23.4	23.7	23.9	23.4	1.2	4.9	1.4	6.0	15	10	100
	N3M	µg/l	16.6	16.1	16.1	16.6	1.9	11.6	1.6	10.2	20	11	100
Ba	A1M	µg/l	15.5	15.0	15.0	15.1	0.8	5.1	0.7	4.5	10	10	100
	D2M	µg/l	5.46	5.46	5.46	5.53	0.29	5.3	0.26	4.8	10	10	100
	N3M	µg/l	38.0	38.0	38.0	38.5	2.0	5.2	1.7	4.6	10	10	100
Ca	A1M	mg/l	17.5	16.9	16.9	17.1	0.9	5.1	0.8	4.6	10	12	82
	D2M	mg/l	18.6	18.6	18.7	18.8	0.7	3.8	0.7	3.7	10	11	100
	N3M	mg/l	8.69	8.69	8.69	8.69	0.37	4.3	0.33	3.8	10	12	100
Cd	A1M	µg/l	0.65	0.65	0.66	0.66	0.04	5.7	0.03	4.5	10	13	92
	D2M	µg/l	0.22	0.22	0.22	0.22	0.01	6.4	0.01	6.0	15	12	91
	N3M	µg/l	0.54	0.54	0.54	0.54	0.03	4.8	0.02	4.3	15	13	91
Co	A1M	µg/l	1.95	1.94	1.94	1.93	0.11	5.5	0.09	4.8	10	11	100
	D2M	µg/l	1.61	1.61	1.61	1.60	0.14	8.5	0.12	7.5	15	10	89
	N3M	µg/l	2.21	2.21	2.21	2.22	0.16	7.4	0.15	6.8	15	11	100
Cr	A1M	µg/l	3.35	3.10	3.09	3.20	0.52	16.8	0.48	15.6	15	12	64
	D2M	µg/l	1.59	1.60	1.51	1.59	0.20	13.2	0.07	4.2	15	11	60
	N3M	µg/l	3.67	3.67	3.62	3.58	0.29	7.9	0.22	5.9	15	12	82
Cu	A1M	µg/l	6.35	6.12	6.19	6.11	0.49	8.0	0.39	6.3	10	13	75
	D2M	µg/l	123	123	123	125	4	3.6	4	3.3	10	12	91
	N3M	µg/l	5.39	5.39	5.44	5.45	0.32	6.0	0.25	4.6	15	13	83
Fe	A1M	µg/l	115	116	116	116	8	6.7	7	5.9	10	13	100
	D2M	µg/l	76.9	78.2	78.2	76.9	6.3	8.1	5.6	7.1	15	12	100
	N3M	µg/l	315	315	316	317	23	7.3	23	7.2	15	13	83
Hg	A1Hg	µg/l	0.064	0.076	0.076	0.070	0.017	22.9	0.015	20.2	25	10	56
	D2Hg	µg/l	0.025	0.027	0.030	0.027	0.006	21.7	0.003	9.5	25	10	67
	N3Hg	µg/l	0.117	0.123	0.129	0.121	0.026	20.4	0.018	14.7	20	10	67
K	A1M	mg/l	1.50	1.52	1.54	1.53	0.04	2.7	0.02	1.3	10	11	100
	D2M	mg/l	1.42	1.42	1.41	1.41	0.03	2.3	0.04	2.5	10	10	100
	N3M	mg/l	2.21	2.21	2.20	2.21	0.03	1.5	0.03	1.1	10	11	100
Mg	A1M	mg/l	7.50	7.28	7.30	7.42	0.35	4.8	0.33	4.6	10	12	91
	D2M	mg/l	1.61	1.59	1.59	1.61	0.08	4.9	0.07	4.7	10	11	100
	N3M	mg/l	3.30	3.30	3.31	3.30	0.14	4.1	0.13	4.0	10	12	100
Mn	A1M	µg/l	9.95	9.38	9.44	9.60	0.75	7.9	0.81	8.7	10	13	75
	D2M	µg/l	11.2	11.2	11.3	11.4	0.7	6.0	0.8	7.0	15	12	91
	N3M	µg/l	6.05	6.05	6.00	6.05	0.39	6.5	0.31	5.1	15	13	92
Mo	A1M	µg/l	11.5	11.9	11.9	12.0	0.9	7.5	0.8	6.7	10	12	82
	D2M	µg/l	5.22	5.22	5.22	5.18	0.23	4.4	0.20	3.9	10	11	100
	N3M	µg/l	12.9	13.1	13.1	12.9	0.8	5.7	0.7	5.1	10	12	91
Na	A1M	mg/l	12.5	12.2	12.2	12.5	0.6	4.9	0.5	4.3	10	12	100
	D2M	mg/l	7.68	7.68	7.68	7.83	0.51	6.6	0.45	5.8	10	11	100
	N3M	mg/l	10.1	10.0	10.0	10.1	0.6	5.6	0.5	5.0	10	12	100

Table 1. The summary of the results in the proficiency test MET 05/2021.

Measurand	Sample	Unit	Assigned value	Mean	Rob. mean	Median	s_{rob}	s_{rob} %	s	s %	2 x s_{pt} %	n_{all}	Acc z % / E_n %
Ni	A1M	µg/l	2.25	2.26	2.18	2.27	0.22	10.2	0.14	6.1	10	12	70
	D2M	µg/l	2.54	2.51	2.51	2.54	0.18	7.2	0.16	6.5	15	11	80
	N3M	µg/l	6.30	6.30	6.29	6.33	0.26	4.1	0.25	3.9	10	12	82
Pb	A1M	µg/l	2.16	2.04	2.04	2.05	0.11	5.5	0.11	5.5	10	12	90
	D2M	µg/l	1.79	1.79	1.79	1.80	0.13	7.2	0.12	6.7	15	11	100
	N3M	µg/l	3.34	3.20	3.20	3.22	0.20	6.3	0.18	5.5	15	12	100
Sb	A1M	µg/l	2.25	2.26	2.24	2.26	0.13	6.0	0.10	4.3	10	10	89
	D2M	µg/l	1.03	1.03	1.03	1.02	0.04	4.3	0.04	3.8	10	10	100
	N3M	µg/l	2.00	2.00	1.89	1.99	0.28	14.6	0.08	4.0	10	10	78
Se	A1M	µg/l	1.25	1.27	1.26	1.25	0.06	4.8	0.06	4.7	15	11	80
	D2M	µg/l	2.10	2.10	2.10	2.11	0.15	6.9	0.13	6.1	15	11	100
	N3M	µg/l	5.15	5.15	5.15	5.16	0.13	2.5	0.12	2.2	10	11	90
Ti	A1M	µg/l	18.5	18.8	18.9	18.9	0.9	4.8	1.0	5.3	10	9	100
	D2M	µg/l	2.36	2.36	-	2.45	-	-	0.26	10.9	-	9	*80*
	N3M	µg/l	28.4	28.4	28.4	29.2	1.7	5.9	1.5	5.2	20	9	88
V	A1M	µg/l	3.35	3.31	3.31	3.34	0.21	6.2	0.18	5.5	10	9	88
	D2M	µg/l	1.56	1.56	1.59	1.58	0.11	6.6	0.07	4.7	15	9	88
	N3M	µg/l	4.83	4.83	4.90	4.92	0.35	7.2	0.24	5.0	15	9	88
Zn	A1M	µg/l	13.5	13.5	13.7	13.5	0.7	4.8	0.4	2.6	10	12	82
	D2M	µg/l	6.53	6.53	6.50	6.43	0.33	5.0	0.35	5.4	15	11	90
	N3M	µg/l	22.7	22.7	23.0	22.6	1.0	4.3	0.5	2.3	10	12	100

Rob. mean: the robust mean, s_{rob}: the robust standard deviation, s_{rob} %: the robust standard deviation as percent, s : standard deviation, s % : the standard deviation as percent, $2\times s_{pt}$ %: the standard deviation for proficiency assessment at the 95 % confidence level, n_{all}: the number of the participants, Acc z %: the results (%), where $|z| \leq 2$, Acc E_n %: the results (%), where $|E_n| \leq 1.0$.

3.2 Analytical methods

The participants could use different analytical methods for the measurements in the PT. The used analytical methods and results of the participants grouped by methods are shown in more detail in Appendix 10. The statistical comparison of the analytical methods was possible for the data where the number of the results was ≥ 5.

Effect of measurement methods on elemental results

Participants used mostly ICP-MS technique followed by ICP-OES technique for the measurements. (Appendix 10). The difference between the average concentrations of metals measured by different measurement methods was tested using the t-test. In the statistical treatment no significant differences were observed, when the number of results was high enough for the statistical comparison. Similarly, by visual comparison of the other results no clear difference was observed.

As a general note, a low recovery may be an indication of loss of measurand which can occur during sample pretreatment (e.g. volatilization during acid digestion). It may also be caused by incorrect background correction (ICP-OES) or matrix effects. Recoveries that are too high may be caused by spectral interferences (overlapping wavelengths in emission spectrometry, polyatomic or isobaric interferences in mass spectrometry), matrix effects or contamination. Matrix effects can often be overcome by matrix matching the calibration standards however this is often difficult with environmental samples since the elemental concentrations vary a lot even within the same sample type.

The most pragmatic approach to minimize matrix effects in ICP techniques is to ensure robust plasma conditions. Appropriate internal standardization should be used, especially with ICP-MS. Matching the ionization potential and mass of the internal standard with those of the analytes is always a compromise. The samples measured in this round had rather clean matrices, therefore not particularly challenging in this respect. ICP-OES typically does not require internal standardization for natural waters, if plasma conditions are robust enough.

In the previous similar PT MET 05/2020 the assessment of boron results was demanding [5]. In this round no similar kind of variation of the boron results were noticed. Boron is poorly ionized in the ICP and is therefore one of the most insensitive elements. In addition, it displays poor wash-out characteristics resulting in a high carry-over. Therefore, it is important to monitor the blank signal at regular intervals during sample measurement. Internal standardization in ICP-MS is also difficult due to the low mass of both boron isotopes. The closest elements in mass, lithium and beryllium, are typically analytes of interest in environmental samples and therefore not suitable. However, enriched ^{6}Li is sometimes used as in internal standard. The neighbouring carbon peak ^{12}C may sometimes cause elevated background signals, as methanol or some other carbon containing substance is often added to the samples on-line to enhance the sensitivity of arsenic and selenium.

According to the results of this PT, most of the participant's results remained lower than the assigned values (calculated value) of As, Ba, Ca, Mg, Mn, Pb for the sample A1M. For Al and K in the sample A1M and for Hg in the sample A1Hg participant's results remained higher than the assigned values. However, the differences were generally within the reported measurement uncertainties of the participants. Both A1M and A1Hg were synthetic samples with no matrix effect present. The participants should pay attention to the calibration procedures and the preparation of calibration solutions to minimize systematic errors. Also, the use of internal standards should be carefully validated for all analytes.

Effect of measurement methods on mercury results

For the analysis of mercury, ICP-MS was the most often used method of analysis. That was followed by CV-AFS. Other used methods were CV-AAS, and CV-ICP-MS (Appendix 10). Due to low number of measurement result, effect of measurement method on Hg results was checked only visually. No differrences were found based on visual estimation.

Like other metal determinations, mercury results are also affected by used digestion procedures (acids and oxidation reagents, their concentration, volumes and purities, digestion temperature and time). For natural water samples hydrochloric acid is recommended for sample preservation and BrCl is recommended for oxidation of mercury species.

Generally, the differences in mercury results are most likely due to different pretreatment procedures, provided a measurement technique sensitive enough is used. Cold vapour techniques are recommended, especially for natural water matrices with low concentrations. CV-AFS and CV-ICP-MS have superior detection capability compared to CV-AAS or CV-ICP-OES.

3.3 Uncertainties of the results

At maximum 85 % of the participants reported the expanded uncertainties (k=2) at least with some of their results (Table 2, Appendix 10). Several approaches were used for estimating the measurement uncertainty (Appendix 11). The most commonly used approach was based on the internal quality from synthetic control sample data with and without sample replicates and the method validation data [6]. MUkit measurement uncertainty software for the estimation of the uncertainties was used by at

maximum two participants (Appendix 11) [6, 7]. The free software is available on the webpage: www.syke.fi/envical/en. Generally, the used approach for estimating measurement uncertainty did not make definite impact on the uncertainty estimates.

The range of the reported uncertainties varied between the measurements and the sample types. As can be seen in Table 2, some of the participants have over-estimated their expanded (k=2) measurement uncertainty. Very high measurement uncertainties (i.e. 50 % or higher, with bold in Table 2) should not exist, unless the measured concentration is near to the limit of quantification. In this PT the participants did not report expanded uncertainties below 5 %, which could commonly be considered unrealistic uncertainty value for routine laboratories.

In order to promote the enhancement of environmental measurements' quality standards and traceability, the national quality recommendations for data entered into the water quality registers have been published in Finland [8]. The recommendation for measurement uncertainties for majority of tested measurands in natural waters is 15 %, except for As it is 0.1 µg/l in sample N3M. For Mn, the recommended uncertainty is 3 µg/l at ca. 10 µg/l concentration level and for Ca, K, Mg, and Na 10 % [8]. In this proficiency test some of the participants had their measurement uncertainties within this limit, while some did not achieve it. However, harmonization of the uncertainties' estimation should be continued.

Table 2. The range of the expanded measurement uncertainties (k=2, U_i%) reported by the participants.

Sample / Measurand	A1M/A1Hg, %	D2M/D2Hg, %	N3M/N3Hg, %
Al	6-25	6-25	6-25
As	10-23	10-23	10-25
B	10-30	10-30	10-30
Ba	10-20	10-30	10-20
Ca	6-32	8-32	6-32
Cd	10-27	10-30	10-27
Co	10-20	10-20	10-20
Cr	10-39	10-39	10-39
Cu	9-20	10-20	9-20
Fe	8-30	10-30	8-30
Hg	15-45	15-**69**	15-30
K	10-23	10-23	10-23
Mg	6-20	10-20	6-20
Mn	8-20	8-20	8-20
Mo	10-20	10-30	10-20
Na	6-20	10-20	6-20
Ni	10-30	10-30	10-30
Pb	10-30	10-30	10-30
Sb	10-30	10-30	10-30
Se	10-30	10-30	10-30
Ti	10-**80**	10-**100**	10-**50**
V	10-30	10-30	10-30
Zn	8-30	8-30	8-30

In table with bold the values of expanded measurement uncertainty 50 % or higher.

4 Evaluation of the results

The performance evaluation of the participants was based on the z and E_n scores (Appendix 6). They were interpreted as follows:

Criteria	Performance
$\lvert z \rvert \leq 2$	Satisfactory
$2 < \lvert z \rvert < 3$	Questionable
$\lvert z \rvert \geq 3$	Unsatisfactory
$-1.0 \leq E_n \leq 1.0$	Satisfactory
$E_n < -1.0$ or $E_n > 1.0$	Unsatisfactory

In total, 90 % of the results evaluated based on the z scores were satisfactory, when deviation 10–20 % from the assigned value was accepted (Appendix 8). Of the results (Ti: D2M) evaluated based on E_n scores 80 % were satisfactory (Appendix 8). Altogether 73 % of participants used accredited analytical methods at least for a part of the measurands and 79 % of their results were satisfactory. The summary of the performance evaluation and comparison to the previous performance is presented in Table 3. In the previous PT, MET 05/2020, the performance was satisfactory for 88 % of the participant results, when deviation 10–30 % from the assigned value was accepted [5]. Further, the measurands here were partly same than in PT MET 04/2019, and thus the performance is partly compared also against those results [9].

Table 3. Summary of the performance evaluation in the proficiency test MET 05/2021.

Sample	Satisfactory results, %	2 x s_{pt}%	Remarks
A1M, A1Hg	86	10-25	• Mainly good performance. • Difficulties in measurements for Al, Cu, Hg, Mn, and Ni: < 80% satisfactory results. • In the previous PTs MET 05/2020 and MET 04/2019 the performance was satisfactory for 94 % and 89 % of the results, when accepting deviation of 10-25 % and 10-20 % from the assigned value, respectively [5, 9].
D2M, D2Hg	z score: 93 E_n score Ti: 80	10-25	• Mainly very good performance based on z scores. • Difficulties in measurements for Cr and Hg: < 80% satisfactory results. • In the previous PT MET 04/2019 the performance was satisfactory for 90 % of the results, when accepting deviation of 15–25 from the assigned value [9].
N3M, N3Hg	90	10–20	• Mainly very good performance. • Difficulties in measurements for As and Hg: < 80% satisfactory results. • In the previous PT MET 05/2020 the performance was satisfactory for 85 % of the results, when accepting deviation of 10–25 from the assigned value [5].

The percentage of the satisfactory results evaluated by the z scores varied between 86 % and 93 % for the tested sample types (Table 3). The share of the satisfactory results in the synthetic sample A1Hg was 56 %. In the sample A1M the share of the satisfactory results was the lowest for Ni, about 70 %, while for As, B, Ba, Co, Fe, K, and Na all results were satisfactory.

For As, B, Ba, Ca, Fe, K, Mg, Mo, Na, Pb, Sb, and Se all results were satisfactory based on z score evaluation in the drinking water sample D2M. The share of the satisfactory results was the lowest for Cu, 60 %, in the sample D2M. For the natural (lake) water sample N3M all results for B, Ba, Ca, Co, K, Mg, Na, Pb, and Zn were satisfactory based on z score evaluation. The share of the satisfactory results was the lowest for Hg, 67 %, in the sample N3M. In this proficiency test the share of the satisfactory results was somewhat higher than in the previous similar proficiency test MET 05/2020 (Table 3) [5].

5 Summary

Proftest SYKE carried out the proficiency test (PT) for analysis of metals in natural and drinking waters in April-May 2021. The measurands for the synthetic sample and drinking as well as natural water samples were: Al, As, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Mg, Mn, Mo, Na, Ni, Pb, Sb, Se, Ti, V, and Zn. In total 15 participants joined in the PT.

The calculated values (NIST traceable) were used as the assigned values for the synthetic samples except for Hg and Pb. For Hg and Pb in the samples AIM, A1Hg, D2M, D2Hg, N3M, and N3Hg the results based on metrologically traceable isotope dilution (ID) ICP-MS technique were used as assigned values. For the other samples and measurands the mean or the median ($n_{stat} < 12$) of the participants' results was used as the assigned value.

The uncertainties of the calculated and the metrologically traceable assigned values for metals in the synthetic samples varied between 0.4 and 3 %. When using the mean or the median of the participant results as the assigned value, the uncertainties of the assigned values varied between 0.8 and 9.7 %.

The evaluation of the performance was based on the z and E_n scores. In this PT, 90 % of the results evaluated based on the z score were satisfactory, when deviation 10–20 % from the assigned value was accepted. Of the results (Ti: D2M) evaluated based on E_n scores 80 % were satisfactory. About 73 % of the participants used accredited methods at least for a part of the measurands and 79 % of their results were satisfactory.

6 Summary in Finnish

Proftest SYKE järjesti ympäristönäytteitä analysoiville laboratorioille pätevyyskokeen huhti-toukokuussa 2021. Pätevyyskokeessa määritettiin synteettisistä näytteistä sekä talous- ja luonnonvesinäytteistä testisuureet Al, As, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Mg, Mn, Mo, Na, Ni, Pb, Sb, Se, Ti, V ja Zn. Pätevyyskokeessa oli yhteensä 15 osallistujaa.

Testisuureen vertailuarvona käytettiin joko laskennallista pitoisuutta tai osallistujien tulosten keskiarvoa tai mediaania. Lyijylle ja elohopealle käytettiin vertailuarvona metrologisesti jäljitettävää pitoisuutta osalla testinäytteistä. Vertailuarvolle laskettiin laajennettu epävarmuus 95 % luottamusvälillä. Vertailuarvon laajennettu epävarmuus oli välillä 0,4–3 % laskennallista tai metrologisesti jäljitettävää pitoisuutta vertailuarvona käytettäessä ja muilla välillä 0,8–9,7 %.

Pätevyyden arviointi tehtiin z- ja E_n- arvojen avulla. Koko aineistossa hyväksyttäviä tuloksia z-arvoilla arvioituna oli 90 %, kun tulosten annettiin vaihdella 10–20 % vertailuarvosta. Talousvesinäytteen D2M titaanin tulokset arvioitiin käyttäen E_n-arvoja ja näistä 80 % oli hyväksyttäviä. Noin 73 % osallistujista käytti akkreditoituja määritysmenetelmiä ja näistä tuloksista oli hyväksyttäviä 79 %.

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Appendix 1. Participants in the proficiency test

Country	Participant
Finland	Eurofins Ahma Oy, Oulu
	Eurofins Environment Testing Finland Oy, Lahti
	KVVY Tutkimus Oy, Tampere
	Kymen Ympäristölaboratorio Oy
	Lounais-Suomen vesi- ja ympäristötutkimus Oy, Turku
	Luonnonvarakeskus, Viikki B2-laboratorio
	MetropoliLab Oy
	Neste Corporation, Technology Center, Kilpilahti
	Neste Oyj, AQC Laadunvalvontalaboratorio, Kulloo
	Savo-Karjalan Ympäristötutkimus Oy, Kuopio
	SeiLab Oy Seinäjoen toimipiste
	SGS Finland Oy, Kotka
	SYKE, Helsingin toimipaikka
Norway	Eurofins Environment Norway A/S, Moss, Norway
Sweden	Stockholm University, ACES

Appendix 2. Sample preparation

The synthetic sample A1M was prepared by diluting from the NIST traceable certified reference materials produced by Inorganic Ventures. The synthetic sample A1Hg was prepared by diluting from the NIST traceable AccuTrace™ Reference Standard produced by AccuStandard, Inc. The water samples D2M and N3M were prepared by adding some separate metal solutions (Merck CertiPUR®) into the original water sample, if the original concentration was not high enough. Samples D2Hg and N3Hg were prepared by adding from the NIST traceable AccuTrace™ Reference Standard produced by AccuStandard, Inc., if the original concentration was not high enough.

Measurand		A1M µg/l	D2M µg/l	N3M µg/l	Measurand		A1M µg/l	D2M µg/l	N3M µg/l
Al	Original	255	3.2	360	**Fe**	Original	1 150	13	255
	Dilution	10	-	-		Dilution	10	-	-
	Addition	-	10	-		Addition	-	62	-
	Ass. value	25.5	14.7	527		Ass. value	115	76.9	315
As	Original	22.5	0.1	0.65	**K**	Original	15 000	1 380	2 140
	Dilution	10	-	-		Dilution	10	-	-
	Addition	-	2	-		Addition	-	-	-
	Ass. value	2.25	2.16	0.64		Ass. value	1 500	1 420	2 210
B	Original	255	10.4	15	**Mg**	Original	75 000	1 610	3 410
	Dilution	10	-	-		Dilution	10	-	-
	Addition	-	10	-		Addition	-	-	-
	Ass. value	25.5	23.4	16.6		Ass. value	7 500	1 610	3 300
Ba	Original	155	5.4	37	**Mn**	Original	99.5	0.9	5.9
	Dilution	10	-	-		Dilution	10	-	-
	Addition	-	-	-		Addition	-	10	-
	Ass. value	15.5	5.46	38.0		Ass. value	9.95	11.2	6.05
Ca	Original	175 000	18 540	8 810	**Mo**	Original	115	< 0.05	0.5
	Dilution	10	-	-		Dilution	10	-	-
	Addition	-	-	-		Addition	-	5	12
	Ass. value	17 500	18 600	8 690		Ass. value	11.5	5.22	12.9
Cd	Original	6.5	< 0.003	0.02	**Na**	Original	125 000	7 650	10 130
	Dilution	10	-	-		Dilution	10	-	-
	Addition	-	0.2	0.5		Addition	-	-	-
	Ass. value	0.65	0.22	0.54		Ass. value	12 500	7 680	10 100
Co	Original	19.5	0.01	0.1	**Ni**	Original	22.5	0.45	1.2
	Dilution	10	-	-		Dilution	10	-	-
	Addition	-	1.5	2		Addition	-	2	5
	Ass. value	1.95	1.61	2.21		Ass. value	2.25	2.54	6.30
Cr	Original	33.5	0.05	0.48	**Pb**	Original	21.5	0.26	0.24
	Dilution	10	-	-		Dilution	10	-	-
	Addition	-	1.5	3		Addition	-	1.76	3
	Ass. value	3.35	1.59	3.67		Ass. value	2.16	1.79	3.34
Cu	Original	63.5	120	4.3	**Sb**	Original	22.5	0.02	0.09
	Dilution	10	-	-		Dilution	10	-	-
	Addition	-	-	-		Addition	-	1	2
	Ass. value	6.35	123	5.39		Ass. value	2.25	1.03	2.00

Measurand		A1M µg/l	D2M µg/l	N3M µg/l	Measurand		A1M µg/l	D2M µg/l	N3M µg/l
Se	Original	12.5	< 0.1	< 0.1	**Zn**	Original	135	6.9	2.4
	Dilution	10	-	-		Dilution	10	-	-
	Addition	-	2	5		Addition	-	-	20
	Ass. value	1.25	2.10	5.15		Ass. value	13.5	6.53	22.7
Ti	Original	185	0.14	13	**Measurand**		**A1Hg µg/l**	**D2Hg µg/l**	**N3Hg µg/l**
	Dilution	10	-	-					
	Addition	-	2	10					
	Ass. value	18.5	2.36	28.4					
V	Original	33.5	0.03	0.67	**Hg**	Original	-	< 0.0005	0.001
	Dilution	10	-	-		Dilution	-	-	-
	Addition	-	1.5	3.89		Addition	0.065	0.025	0.119
	Ass. value	3.35	1.56	4.83		Ass. value	0.064	0.025	0.117

Original = the original concentration
Dilution = the ratio of dilution
Addition = the addition concentration
Ass. value = the assigned value

Appendix 3. Homogeneity of the samples

Homogeneity was tested from replicate measurements of selected measurement from three samples of each sample type.

Criteria for homogeneity:

$s_{anal}/s_h < 0.5$ and $s_{sam}^2 < c$, where

s_h = standard deviation for proficiency assessment
s_{anal} = analytical deviation, standard deviation of the results in a sub sample
s_{sam} = between-sample deviation, standard deviation of the results between sub samples

$c = F1 \times s_{all}^2 + F2 \times s_{anal}^2$, where
$s_{all}^2 = (0.3 \times s_h)^2$

F1 and F2 are constants of F distribution derived from the standard statistical tables for the tested number of samples [2, 3].

Measurand/Sample	Concentration [µg/l]	n	s_{pt} %	s_h%	s_h	s_{anal}	s_{anal}/s_h	s_{anal}/s_h<0.5?	s_{sam}^2	c	s_{sam}^2<c?
Cd/D2M	0.21	3	7.5	2.5	0.005	0.0007	0.13	Yes	0.000009	0.00001	Yes
Cr/D2M	1.57	3	7.5	1.0	0.02	0.008	0.50	Yes	0.00002	0.0003	Yes
Pb/D2M	1.81	3	7.5	1.1	0.02	0.009	0.48	Yes	0.00008	0.0005	Yes
Se/D2M	2.08	3	7.5	3.4	0.07	0.04	0.50	Yes	0	0.007	Yes
Zn/D2M	6.52	3	7.5	1.3	0.08	0.04	0.48	Yes	0.001	0.009	Yes
Cd/N3M	0.55	3	7.5	4.9	0.03	0.01	0.50	Yes	0	0.001	Yes
Cr/N3M	3.66	3	7.5	0.7	0.03	0.01	0.49	Yes	0.0005	0.0008	Yes
Pb/N3M	3.32	3	7.5	1.2	0.04	0.02	0.48	Yes	0	0.002	Yes
Se/N3M	5.29	3	5	1.7	0.09	0.04	0.49	Yes	0	0.01	Yes
Zn/n3M	22.8	3	5	1.4	0.32	0.15	0.47	Yes	0.01	0.12	Yes
Hg/D2Hg*	0.02	3	12.5	0.9	0.0002	0.0001	0.45	Yes	0	00000001	Yes
Hg/N3Hg*	0.12	3	10	1.0	0.001	0.0006	0.49	Yes	0	0.000002	Yes
Pb/D2M*	1.78	3	7.5	2.0	0.04	0.02	0.49	Yes	0.0001	0.002	Yes
Pb/N3M*	3.34	2	7.5	0.4	0.01	0.006	0.47	Yes	0	0.0002	Yes

* result based on the ID-ICP-MS measurement; s_{pt} % = standard deviation for proficiency assessment

Conclusion: All criteria for homogeneity were fulfilled and the samples could be considered homogenous.

Appendix 4. Feedback from the proficiency test

FEEDBACK FROM THE PARTICIPANTS

Participant	Comments on technical excecution	Action / Proftest SYKE
11	The participant received the samples one day after the estimated delivery day.	TNT had difficulties with the international deliveries.

Participant	Comments to the results	Action / Proftest SYKE
16	The participant had access problems with their result sheet.	The participant made the PT registration with their permanent laboratory code, but informed that they need a new laboratory code. The change of the laboratory code caused difficulties for the result reporting. The problem was fixed by the provider and the participant was informed. Provider apologized the problem.
4	The participant did not report their results within the given timetable. Participant informed that they did not had access to the ProftestWEB during the day of reporting deadline 7th May, 2021.	The provider contacted the participant on 10th May, 2021 and updated the timetable for reporting. Unfortunately, the participant had no time to report within the new timetable. Therefore, those results are in this report, but they are not included in the statistical processing of the data and the results were not evaluated. The participant can evaluate their performance, and more information is available available from the Guide for participant [4].

FEEDBACK TO THE PARTICIPANTS

Participant	Comments
3	The participant reported value 0 µg/l for Cd in the sample D2M. This result was removed from the statistical handling.
14	The participant reported their results for Ni in the sample A1M below detection limit <2 µg/l. The assigned value was 2.25 µg/l. The provider recommends the participant to re-evaluate the detection limit.

Appendix 5. Evaluation of the assigned values and their uncertainties

Measurand	Sample	Unit	Assigned value	U_{pt}	U_{pt}, %	Evaluation method of assigned value	u_{pt}/s_{pt}
Al	A1M	µg/l	25.5	0.2	0.6	Calculated value	0.03
	D2M	µg/l	14.7	1.0	6.8	Median	0.34
	N3M	µg/l	527	32	6.1	Median	0.31
As	A1M	µg/l	2.25	0.02	0.8	Calculated value	0.05
	D2M	µg/l	2.16	0.07	3.4	Median	0.34
	N3M	µg/l	0.64	0.02	3.3	Median	0.33
B	A1M	µg/l	25.5	0.2	0.8	Calculated value	0.05
	D2M	µg/l	23.4	0.9	4.0	Median	0.27
	N3M	µg/l	16.6	1.2	7.2	Median	0.36
Ba	A1M	µg/l	15.5	0.1	0.6	Calculated value	0.06
	D2M	µg/l	5.46	0.17	3.1	Mean	0.31
	N3M	µg/l	38.0	1.2	3.1	Mean	0.31
Ca	A1M	mg/l	17.5	0.1	0.5	Calculated value	0.05
	D2M	mg/l	18.6	0.4	2.3	Mean	0.23
	N3M	mg/l	8.69	0.20	2.3	Mean	0.23
Cd	A1M	µg/l	0.65	0.00	0.6	Calculated value	0.06
	D2M	µg/l	0.22	0.01	3.8	Mean	0.25
	N3M	µg/l	0.54	0.01	2.7	Mean	0.18
Co	A1M	µg/l	1.95	0.01	0.6	Calculated value	0.06
	D2M	µg/l	1.61	0.09	5.3	Mean	0.35
	N3M	µg/l	2.21	0.10	4.3	Mean	0.29
Cr	A1M	µg/l	3.35	0.02	0.6	Calculated value	0.04
	D2M	µg/l	1.59	0.05	3.4	Median	0.23
	N3M	µg/l	3.67	0.14	3.9	Mean	0.26
Cu	A1M	µg/l	6.35	0.04	0.7	Calculated value	0.07
	D2M	µg/l	123	3	2.1	Mean	0.21
	N3M	µg/l	5.39	0.16	2.9	Mean	0.19
Fe	A1M	µg/l	115	1	0.7	Calculated value	0.07
	D2M	µg/l	76.9	3.3	4.3	Median	0.29
	N3M	µg/l	315	14	4.5	Mean	0.30
Hg	A1Hg	µg/l	0.064	0.002	3.0	ID-ICP-MS	0.12
	D2Hg	µg/l	0.025	0.001	3.0	ID-ICP-MS	0.12
	N3Hg	µg/l	0.117	0.004	3.0	ID-ICP-MS	0.15
K	A1M	mg/l	1.50	0.01	0.6	Calculated value	0.06
	D2M	mg/l	1.42	0.02	1.7	Mean	0.17
	N3M	mg/l	2.21	0.02	0.8	Mean	0.08
Mg	A1M	mg/l	7.50	0.03	0.4	Calculated value	0.04
	D2M	mg/l	1.61	0.05	2.9	Median	0.29
	N3M	mg/l	3.30	0.08	2.4	Mean	0.24
Mn	A1M	µg/l	9.95	0.07	0.7	Calculated value	0.07
	D2M	µg/l	11.2	0.5	4.2	Mean	0.28
	N3M	µg/l	6.05	0.19	3.1	Mean	0.21
Mo	A1M	µg/l	11.5	0.1	0.6	Calculated value	0.06
	D2M	µg/l	5.22	0.13	2.5	Mean	0.25
	N3M	µg/l	12.9	0.4	3.1	Median	0.31

Measurand	Sample	Unit	Assigned value	U_{pt}	U_{pt}, %	Evaluation method of assigned value	u_{pt}/s_{pt}
Na	A1M	mg/l	12.5	0.1	0.5	Calculated value	0.05
	D2M	mg/l	7.68	0.28	3.7	Mean	0.37
	N3M	mg/l	10.1	0.3	3.0	Median	0.30
Ni	A1M	µg/l	2.25	0.01	0.6	Calculated value	0.06
	D2M	µg/l	2.54	0.12	4.6	Median	0.31
	N3M	µg/l	6.30	0.16	2.6	Mean	0.26
Pb	A1M	µg/l	2.16	0.05	2.5	ID-ICP-MS	0.25
	D2M	µg/l	1.79	0.04	2.5	ID-ICP-MS	0.17
	N3M	µg/l	3.34	0.08	2.5	ID-ICP-MS	0.17
Sb	A1M	µg/l	2.25	0.02	0.8	Calculated value	0.08
	D2M	µg/l	1.03	0.03	2.5	Mean	0.25
	N3M	µg/l	2.00	0.06	3.0	Mean	0.30
Se	A1M	µg/l	1.25	0.01	0.7	Calculated value	0.05
	D2M	µg/l	2.10	0.08	3.9	Mean	0.26
	N3M	µg/l	5.15	0.08	1.5	Mean	0.15
Ti	A1M	µg/l	18.5	0.1	0.7	Calculated value	0.07
	D2M	µg/l	2.36	0.23	9.7	Mean	
	N3M	µg/l	28.4	1.1	3.9	Mean	0.20
V	A1M	µg/l	3.35	0.02	0.6	Calculated value	0.06
	D2M	µg/l	1.56	0.05	3.5	Mean	0.23
	N3M	µg/l	4.83	0.18	3.8	Mean	0.25
Zn	A1M	µg/l	13.5	0.1	0.5	Calculated value	0.05
	D2M	µg/l	6.53	0.24	3.6	Mean	0.24
	N3M	µg/l	22.7	0.4	1.6	Mean	0.16

U_{pt} = Expanded uncertainty of the assigned value
Criterion for reliability of the assigned value $u_{pt}/s_{pt} \leq 0.3$, where
s_{pt}= the standard deviation for proficiency assessment
u_{pt}= the standard uncertainty of the assigned value

If $u_{pt}/s_{pt} \leq 0.3$, the assigned value is reliable.

Appendix 6. Terms in the results tables

The information could be applied according to the PT.

Measurand The tested parameter

Sample The code of the sample

Assigned value The value attributed to a particular property of a proficiency test item

Participant's result The result reported by the participant (when replicate results are reported, the mean value)

2 × s_{pt} % The standard deviation for proficiency assessment (s_{pt}) at the 95 % confidence level

z score Used for the participant's perfomance evaluation in the PT.
Calculated with formula:

$$z = (x_i - x_{pt})/s_{pt}, \text{ where}$$

x_i = the result of the individual participant
x_{pt} = the assigned value
s_{pt} = the standard deviation for proficiency assessment

Interpretation of the z scores

$\lvert z \rvert \leq 2$	Satisfactory
$2 < \lvert z \rvert < 3$	Questionable (warning signal), the result deviates more than 2 × s_{pt} from the assigned value.
$\lvert z \rvert \geq 3$	Unsatisfactory (action signal), the result deviates more than 3 × s_{pt} from the assigned value.

E_n score Error, normalized – Used to evaluate the difference between the assigned value and participant's result within their claimed expanded uncertainty. Calculated with formula:

$$(E_n)_i = \frac{x_i - x_{pt}}{\sqrt{U_i^2 + U_{pt}^2}}, \text{ where}$$

U_i = the expanded uncertainty of a participant's result
U_{pt} = the expanded uncertainty of the assigned value

Interpretation of the E_n scores

$\lvert E_n \rvert \leq 1.0$	Satisfactory, should be taken as an indicator of successful performance when the uncertainties are valid.
$\lvert E_n \rvert > 1.0$	Unsatisfactory (action signal), could indicate a need to review the uncertainty estimates, or to correct a measurement issue.

Md Median

s Standard deviation

s % Standard deviation, %

n_{stat} Number of results in statistical processing

More information of the statistical calculations in international standards ISO/IEC 17043 and ISO 13528 as well as in Proftest SYKE Guide for participants [1, 2, 4].

Appendix 7. Results of each participant

Participant 1												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Al	µg/l	A1M		1.65	25.5	20	29.7	28.2	28.2	2.0	7.2	10
	µg/l	D2M		0.41	14.7	20	15.3	14.7	14.8	1.7	11.3	11
	µg/l	N3M		-3.61	527	20	337	527	515	52	10.2	11
As	µg/l	A1M		-0.65	2.25	15	2.14	2.14	2.11	0.11	5.4	9
	µg/l	D2M		0.37	2.16	10	2.20	2.16	2.17	0.11	5.1	9
	µg/l	N3M		-1.03	0.64	10	0.61	0.64	0.62	0.03	4.7	8
B	µg/l	A1M		-1.15	25.5	15	23.3	26.9	26.5	1.9	7.3	10
	µg/l	D2M		-1.65	23.4	15	20.5	23.4	23.7	1.4	6.0	9
	µg/l	N3M		-1.51	16.6	20	14.1	16.6	16.1	1.6	10.2	8
Ba	µg/l	A1M		-0.13	15.5	10	15.4	15.1	15.0	0.7	4.5	9
	µg/l	D2M		0.62	5.46	10	5.63	5.53	5.46	0.26	4.8	9
	µg/l	N3M		-0.53	38.0	10	37.0	38.5	38.0	1.7	4.6	9
Ca	mg/l	A1M		0.00	17.5	10	17.5	17.1	16.9	0.8	4.6	11
	mg/l	D2M		0.65	18.6	10	19.2	18.8	18.6	0.7	3.7	10
	mg/l	N3M		0.78	8.69	10	9.03	8.69	8.69	0.33	3.8	11
Cd	µg/l	A1M		0.31	0.65	10	0.66	0.66	0.65	0.03	4.5	11
	µg/l	D2M		-1.76	0.22	15	0.19	0.22	0.22	0.01	6.0	10
	µg/l	N3M		-0.15	0.54	15	0.53	0.54	0.54	0.02	4.3	10
Co	µg/l	A1M		-0.10	1.95	10	1.94	1.93	1.94	0.09	4.8	10
	µg/l	D2M		-0.17	1.61	15	1.59	1.60	1.61	0.12	7.5	8
	µg/l	N3M		0.06	2.21	15	2.22	2.22	2.21	0.15	6.8	10
Cr	µg/l	A1M		-0.16	3.35	15	3.31	3.20	3.10	0.48	15.6	11
	µg/l	D2M		-0.08	1.59	15	1.58	1.59	1.60	0.07	4.2	6
	µg/l	N3M		-0.69	3.67	15	3.48	3.58	3.67	0.22	5.9	9
Cu	µg/l	A1M		0.00	6.35	10	6.35	6.11	6.12	0.39	6.3	11
	µg/l	D2M		0.49	123	10	126	125	123	4	3.3	10
	µg/l	N3M		-0.25	5.39	15	5.29	5.45	5.39	0.25	4.6	10
Fe	µg/l	A1M		-0.35	115	10	113	116	116	7	5.9	12
	µg/l	D2M		-0.36	76.9	15	74.8	76.9	78.2	5.6	7.1	11
	µg/l	N3M		-3.09	315	15	242	317	315	23	7.2	10
Hg	µg/l	A1Hg		-0.20	0.064	25	0.062	0.070	0.076	0.015	20.2	8
	µg/l	D2Hg		-0.54	0.025	25	0.023	0.027	0.027	0.003	9.5	6
	µg/l	N3Hg		-0.51	0.117	20	0.111	0.121	0.123	0.018	14.7	7
K	mg/l	A1M		1.33	1.50	10	1.60	1.53	1.52	0.02	1.3	8
	mg/l	D2M		0.42	1.42	10	1.45	1.41	1.42	0.04	2.5	9
	mg/l	N3M		0.09	2.21	10	2.22	2.21	2.21	0.03	1.1	9
Mg	mg/l	A1M		-0.61	7.50	10	7.27	7.42	7.28	0.33	4.6	11
	mg/l	D2M		0.75	1.61	10	1.67	1.61	1.59	0.07	4.7	10
	mg/l	N3M		0.91	3.30	10	3.45	3.30	3.30	0.13	4.0	11
Mn	µg/l	A1M		-0.06	9.95	10	9.92	9.60	9.38	0.81	8.7	12
	µg/l	D2M		0.24	11.2	15	11.4	11.4	11.2	0.8	7.0	11
	µg/l	N3M		-0.29	6.05	15	5.92	6.05	6.05	0.31	5.1	11
Mo	µg/l	A1M		-0.52	11.5	10	11.2	12.0	11.9	0.8	6.7	11
	µg/l	D2M		-0.80	5.22	10	5.01	5.18	5.22	0.20	3.9	10
	µg/l	N3M		-0.47	12.9	10	12.6	12.9	13.1	0.7	5.1	11

Participant 1												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Na	mg/l	A1M		-1.44	12.5	10	11.6	12.5	12.2	0.5	4.3	11
	mg/l	D2M		-1.17	7.68	10	7.23	7.83	7.68	0.45	5.8	10
	mg/l	N3M		-1.68	10.1	10	9.3	10.1	10.0	0.5	5.0	11
Ni	µg/l	A1M		0.98	2.25	10	2.36	2.27	2.26	0.14	6.1	8
	µg/l	D2M		0.58	2.54	15	2.65	2.54	2.51	0.16	6.5	8
	µg/l	N3M		0.10	6.30	10	6.33	6.33	6.30	0.25	3.9	9
Pb	µg/l	A1M		-0.65	2.16	10	2.09	2.05	2.04	0.11	5.5	10
	µg/l	D2M		0.07	1.79	15	1.80	1.80	1.79	0.12	6.7	10
	µg/l	N3M		-0.36	3.34	15	3.25	3.22	3.20	0.18	5.5	10
Sb	µg/l	A1M		1.42	2.25	10	2.41	2.26	2.26	0.10	4.3	8
	µg/l	D2M		1.36	1.03	10	1.10	1.02	1.03	0.04	3.8	9
	µg/l	N3M		-5.20	2.00	10	1.48	1.99	2.00	0.08	4.0	7
Se	µg/l	A1M		0.43	1.25	15	1.29	1.25	1.27	0.06	4.7	8
	µg/l	D2M		0.00	2.10	15	2.10	2.11	2.10	0.13	6.1	10
	µg/l	N3M		0.12	5.15	10	5.18	5.16	5.15	0.12	2.2	9
Ti	µg/l	A1M		1.51	18.5	10	19.9	18.9	18.8	1.0	5.3	8
	µg/l	D2M			2.36		2.46	2.45	2.36	0.26	10.9	5
	µg/l	N3M		-2.39	28.4	20	21.6	29.2	28.4	1.5	5.2	7
V	µg/l	A1M		-0.24	3.35	10	3.31	3.34	3.31	0.18	5.5	8
	µg/l	D2M		-0.34	1.56	15	1.52	1.58	1.56	0.07	4.7	7
	µg/l	N3M		-0.83	4.83	15	4.53	4.92	4.83	0.24	5.0	7
Zn	µg/l	A1M		0.15	13.5	10	13.6	13.5	13.5	0.4	2.6	9
	µg/l	D2M		-0.31	6.53	15	6.38	6.43	6.53	0.35	5.4	9
	µg/l	N3M		-0.09	22.7	10	22.6	22.6	22.7	0.5	2.3	9

Participant 2												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Al	µg/l	A1M		0.86	25.5	20	27.7	28.2	28.2	2.0	7.2	10
	µg/l	D2M		-0.07	14.7	20	14.6	14.7	14.8	1.7	11.3	11
	µg/l	N3M		0.49	527	20	553	527	515	52	10.2	11
As	µg/l	A1M		0.12	2.25	15	2.27	2.14	2.11	0.11	5.4	9
	µg/l	D2M		1.39	2.16	10	2.31	2.16	2.17	0.11	5.1	9
	µg/l	N3M		0.44	0.64	10	0.65	0.64	0.62	0.03	4.7	8
B	µg/l	A1M		0.89	25.5	15	27.2	26.9	26.5	1.9	7.3	10
	µg/l	D2M		0.80	23.4	15	24.8	23.4	23.7	1.4	6.0	9
	µg/l	N3M		0.90	16.6	20	18.1	16.6	16.1	1.6	10.2	8
Ba	µg/l	A1M		-0.52	15.5	10	15.1	15.1	15.0	0.7	4.5	9
	µg/l	D2M		0.26	5.46	10	5.53	5.53	5.46	0.26	4.8	9
	µg/l	N3M		0.26	38.0	10	38.5	38.5	38.0	1.7	4.6	9
Ca	mg/l	A1M		-0.46	17.5	10	17.1	17.1	16.9	0.8	4.6	11
	mg/l	D2M		0.22	18.6	10	18.8	18.8	18.6	0.7	3.7	10
	mg/l	N3M		-0.14	8.69	10	8.63	8.69	8.69	0.33	3.8	11
Cd	µg/l	A1M		0.77	0.65	10	0.68	0.66	0.65	0.03	4.5	11
	µg/l	D2M		-0.06	0.22	15	0.22	0.22	0.22	0.01	6.0	10
	µg/l	N3M		0.96	0.54	15	0.58	0.54	0.54	0.02	4.3	10
Co	µg/l	A1M		-0.31	1.95	10	1.92	1.93	1.94	0.09	4.8	10
	µg/l	D2M		-0.41	1.61	15	1.56	1.60	1.61	0.12	7.5	8
	µg/l	N3M		0.06	2.21	15	2.22	2.22	2.21	0.15	6.8	10

Participant 2												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Cr	µg/l	A1M		-0.08	3.35	15	3.33	3.20	3.10	0.48	15.6	11
	µg/l	D2M		0.25	1.59	15	1.62	1.59	1.60	0.07	4.2	6
	µg/l	N3M		0.47	3.67	15	3.80	3.58	3.67	0.22	5.9	9
Cu	µg/l	A1M		-0.94	6.35	10	6.05	6.11	6.12	0.39	6.3	11
	µg/l	D2M		0.00	123	10	123	125	123	4	3.3	10
	µg/l	N3M		0.07	5.39	15	5.42	5.45	5.39	0.25	4.6	10
Fe	µg/l	A1M		-0.35	115	10	113	116	116	7	5.9	12
	µg/l	D2M		-0.33	76.9	15	75.0	76.9	78.2	5.6	7.1	11
	µg/l	N3M		0.17	315	15	319	317	315	23	7.2	10
Hg	µg/l	A1Hg		0.10	0.064	25	0.065	0.070	0.076	0.015	20.2	8
	µg/l	D2Hg		0.10	0.025	25	0.025	0.027	0.027	0.003	9.5	6
	µg/l	N3Hg		0.00	0.117	20	0.117	0.121	0.123	0.018	14.7	7
K	mg/l	A1M		0.40	1.50	10	1.53	1.53	1.52	0.02	1.3	8
	mg/l	D2M		0.00	1.42	10	1.42	1.41	1.42	0.04	2.5	9
	mg/l	N3M		0.18	2.21	10	2.23	2.21	2.21	0.03	1.1	9
Mg	mg/l	A1M		-0.21	7.50	10	7.42	7.42	7.28	0.33	4.6	11
	mg/l	D2M		-0.12	1.61	10	1.60	1.61	1.59	0.07	4.7	10
	mg/l	N3M		0.30	3.30	10	3.35	3.30	3.30	0.13	4.0	11
Mn	µg/l	A1M		-0.76	9.95	10	9.57	9.60	9.38	0.81	8.7	12
	µg/l	D2M		0.12	11.2	15	11.3	11.4	11.2	0.8	7.0	11
	µg/l	N3M		0.26	6.05	15	6.17	6.05	6.05	0.31	5.1	11
Mo	µg/l	A1M		1.22	11.5	10	12.2	12.0	11.9	0.8	6.7	11
	µg/l	D2M		0.80	5.22	10	5.43	5.18	5.22	0.20	3.9	10
	µg/l	N3M		1.40	12.9	10	13.8	12.9	13.1	0.7	5.1	11
Na	mg/l	A1M		0.32	12.5	10	12.7	12.5	12.2	0.5	4.3	11
	mg/l	D2M		0.60	7.68	10	7.91	7.83	7.68	0.45	5.8	10
	mg/l	N3M		0.59	10.1	10	10.4	10.1	10.0	0.5	5.0	11
Ni	µg/l	A1M		0.18	2.25	10	2.27	2.27	2.26	0.14	6.1	8
	µg/l	D2M		0.10	2.54	15	2.56	2.54	2.51	0.16	6.5	8
	µg/l	N3M		0.06	6.30	10	6.32	6.33	6.30	0.25	3.9	9
Pb	µg/l	A1M		-0.74	2.16	10	2.08	2.05	2.04	0.11	5.5	10
	µg/l	D2M		0.07	1.79	15	1.80	1.80	1.79	0.12	6.7	10
	µg/l	N3M		-0.12	3.34	15	3.31	3.22	3.20	0.18	5.5	10
Sb	µg/l	A1M		0.98	2.25	10	2.36	2.26	2.26	0.10	4.3	8
	µg/l	D2M		0.78	1.03	10	1.07	1.02	1.03	0.04	3.8	9
	µg/l	N3M		1.20	2.00	10	2.12	1.99	2.00	0.08	4.0	7
Se	µg/l	A1M		0.75	1.25	15	1.32	1.25	1.27	0.06	4.7	8
	µg/l	D2M		0.06	2.10	15	2.11	2.11	2.10	0.13	6.1	10
	µg/l	N3M		0.62	5.15	10	5.31	5.16	5.15	0.12	2.2	9
Ti	µg/l	A1M		-0.32	18.5	10	18.2	18.9	18.8	1.0	5.3	8
	µg/l	D2M			2.36		2.22	2.45	2.36	0.26	10.9	5
	µg/l	N3M		0.28	28.4	20	29.2	29.2	28.4	1.5	5.2	7
V	µg/l	A1M		0.42	3.35	10	3.42	3.34	3.31	0.18	5.5	8
	µg/l	D2M		0.17	1.56	15	1.58	1.58	1.56	0.07	4.7	7
	µg/l	N3M		0.28	4.83	15	4.93	4.92	4.83	0.24	5.0	7
Zn	µg/l	A1M		0.59	13.5	10	13.9	13.5	13.5	0.4	2.6	9
	µg/l	D2M		0.12	6.53	15	6.59	6.43	6.53	0.35	5.4	9
	µg/l	N3M		0.70	22.7	10	23.5	22.6	22.7	0.5	2.3	9

Participant 3												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Al	µg/l	A1M		2.55	25.5	20	32.0	28.2	28.2	2.0	7.2	10
	µg/l	D2M		0.54	14.7	20	15.5	14.7	14.8	1.7	11.3	11
	µg/l	N3M		0.13	527	20	534	527	515	52	10.2	11
As	µg/l	A1M		-1.48	2.25	15	2.00	2.14	2.11	0.11	5.4	9
	µg/l	D2M		-1.48	2.16	10	2.00	2.16	2.17	0.11	5.1	9
	µg/l	N3M		11.25	0.64	10	1.00	0.64	0.62	0.03	4.7	8
B	µg/l	A1M		0.78	25.5	15	27.0	26.9	26.5	1.9	7.3	10
	µg/l	D2M		0.91	23.4	15	25.0	23.4	23.7	1.4	6.0	9
	µg/l	N3M		-0.36	16.6	20	16.0	16.6	16.1	1.6	10.2	8
Ba	µg/l	A1M		-1.94	15.5	10	14.0	15.1	15.0	0.7	4.5	9
	µg/l	D2M		-1.68	5.46	10	5.00	5.53	5.46	0.26	4.8	9
	µg/l	N3M		-1.05	38.0	10	36.0	38.5	38.0	1.7	4.6	9
Ca	mg/l	A1M		-0.46	17.5	10	17.1	17.1	16.9	0.8	4.6	11
	mg/l	D2M		0.11	18.6	10	18.7	18.8	18.6	0.7	3.7	10
	mg/l	N3M		-0.05	8.69	10	8.67	8.69	8.69	0.33	3.8	11
Cd	µg/l	A1M		10.77	0.65	10	1.00	0.66	0.65	0.03	4.5	11
	µg/l	D2M		-13.33	0.22	15	0.00	0.22	0.22	0.01	6.0	10
	µg/l	N3M		11.36	0.54	15	1.00	0.54	0.54	0.02	4.3	10
Co	µg/l	A1M		0.51	1.95	10	2.00	1.93	1.94	0.09	4.8	10
	µg/l	D2M		-5.05	1.61	15	1.00	1.60	1.61	0.12	7.5	8
	µg/l	N3M		-1.27	2.21	15	2.00	2.22	2.21	0.15	6.8	10
Cr	µg/l	A1M		2.59	3.35	15	4.00	3.20	3.10	0.48	15.6	11
	µg/l	D2M		3.44	1.59	15	2.00	1.59	1.60	0.07	4.2	6
	µg/l	N3M		1.20	3.67	15	4.00	3.58	3.67	0.22	5.9	9
Cu	µg/l	A1M		-1.10	6.35	10	6.00	6.11	6.12	0.39	6.3	11
	µg/l	D2M		0.49	123	10	126	125	123	4	3.3	10
	µg/l	N3M		-0.96	5.39	15	5.00	5.45	5.39	0.25	4.6	10
Fe	µg/l	A1M		0.87	115	10	120	116	116	7	5.9	12
	µg/l	D2M		-0.69	76.9	15	72.9	76.9	78.2	5.6	7.1	11
	µg/l	N3M		0.00	315	15	315	317	315	23	7.2	10
K	mg/l	A1M		0.44	1.50	10	1.53	1.53	1.52	0.02	1.3	8
	mg/l	D2M		-0.46	1.42	10	1.39	1.41	1.42	0.04	2.5	9
	mg/l	N3M		-0.26	2.21	10	2.18	2.21	2.21	0.03	1.1	9
Mg	mg/l	A1M		-0.05	7.50	10	7.48	7.42	7.28	0.33	4.6	11
	mg/l	D2M		0.00	1.61	10	1.61	1.61	1.59	0.07	4.7	10
	mg/l	N3M		0.00	3.30	10	3.30	3.30	3.30	0.13	4.0	11
Mn	µg/l	A1M		-1.91	9.95	10	9.00	9.60	9.38	0.81	8.7	12
	µg/l	D2M		-0.24	11.2	15	11.0	11.4	11.2	0.8	7.0	11
	µg/l	N3M		-0.11	6.05	15	6.00	6.05	6.05	0.31	5.1	11
Mo	µg/l	A1M		0.87	11.5	10	12.0	12.0	11.9	0.8	6.7	11
	µg/l	D2M		-0.84	5.22	10	5.00	5.18	5.22	0.20	3.9	10
	µg/l	N3M		0.16	12.9	10	13.0	12.9	13.1	0.7	5.1	11
Na	mg/l	A1M		0.00	12.5	10	12.5	12.5	12.2	0.5	4.3	11
	mg/l	D2M		0.24	7.68	10	7.77	7.83	7.68	0.45	5.8	10
	mg/l	N3M		-0.02	10.1	10	10.1	10.1	10.0	0.5	5.0	11

Participant 3												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Ni	µg/l	A1M		-2.22	2.25	10	2.00	2.27	2.26	0.14	6.1	8
	µg/l	D2M		2.41	2.54	15	3.00	2.54	2.51	0.16	6.5	8
	µg/l	N3M		-0.95	6.30	10	6.00	6.33	6.30	0.25	3.9	9
Pb	µg/l	A1M		-1.48	2.16	10	2.00	2.05	2.04	0.11	5.5	10
	µg/l	D2M		1.56	1.79	15	2.00	1.80	1.79	0.12	6.7	10
	µg/l	N3M		-1.36	3.34	15	3.00	3.22	3.20	0.18	5.5	10
Sb	µg/l	A1M		-11.11	2.25	10	1.00	2.26	2.26	0.10	4.3	8
	µg/l	D2M		-0.58	1.03	10	1.00	1.02	1.03	0.04	3.8	9
	µg/l	N3M		-10.00	2.00	10	1.00	1.99	2.00	0.08	4.0	7
Se	µg/l	A1M		-2.67	1.25	15	1.00	1.25	1.27	0.06	4.7	8
	µg/l	D2M		-0.63	2.10	15	2.00	2.11	2.10	0.13	6.1	10
	µg/l	N3M		-0.58	5.15	10	5.00	5.16	5.15	0.12	2.2	9
Ti	µg/l	A1M		0.54	18.5	10	19.0	18.9	18.8	1.0	5.3	8
	µg/l	D2M			2.36		2.00	2.45	2.36	0.26	10.9	5
	µg/l	N3M		-0.85	28.4	20	26.0	29.2	28.4	1.5	5.2	7
V	µg/l	A1M		-2.09	3.35	10	3.00	3.34	3.31	0.18	5.5	8
	µg/l	D2M		3.76	1.56	15	2.00	1.58	1.56	0.07	4.7	7
	µg/l	N3M		3.23	4.83	15	6.00	4.92	4.83	0.24	5.0	7
Zn	µg/l	A1M		-0.74	13.5	10	13.0	13.5	13.5	0.4	2.6	9
	µg/l	D2M		-1.08	6.53	15	6.00	6.43	6.53	0.35	5.4	9
	µg/l	N3M		-0.62	22.7	10	22.0	22.6	22.7	0.5	2.3	9

Participant 4												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Al	µg/l	A1M			25.5	20	*27.092*	28.2	28.2	2.0	7.2	10
	µg/l	D2M			14.7	20	*13.716*	14.7	14.8	1.7	11.3	11
	µg/l	N3M			527	20	*438.17*	527	515	52	10.2	11
As	µg/l	A1M			2.25	15	*2.083*	2.14	2.11	0.11	5.4	9
	µg/l	D2M			2.16	10	*2.12*	2.16	2.17	0.11	5.1	9
	µg/l	N3M			0.64	10	*0.593*	0.64	0.62	0.03	4.7	8
B	µg/l	A1M			25.5	15	*22.135*	26.9	26.5	1.9	7.3	10
	µg/l	D2M			23.4	15	*20.749*	23.4	23.7	1.4	6.0	9
	µg/l	N3M			16.6	20	*14.882*	16.6	16.1	1.6	10.2	8
Ba	µg/l	A1M			15.5	10	*14.875*	15.1	15.0	0.7	4.5	9
	µg/l	D2M			5.46	10	*5.457*	5.53	5.46	0.26	4.8	9
	µg/l	N3M			38.0	10	*40.257*	38.5	38.0	1.7	4.6	9
Ca	mg/l	A1M			17.5	10	*15.53*	17.1	16.9	0.8	4.6	11
	mg/l	D2M			18.6	10	*19.012*	18.8	18.6	0.7	3.7	10
	mg/l	N3M			8.69	10	*8.915*	8.69	8.69	0.33	3.8	11
Cd	µg/l	A1M			0.65	10	*0.592*	0.66	0.65	0.03	4.5	11
	µg/l	D2M			0.22	15	*0.199*	0.22	0.22	0.01	6.0	10
	µg/l	N3M			0.54	15	*0.501*	0.54	0.54	0.02	4.3	10
Co	µg/l	A1M			1.95	10	*1.877*	1.93	1.94	0.09	4.8	10
	µg/l	D2M			1.61	15	*1.526*	1.60	1.61	0.12	7.5	8
	µg/l	N3M			2.21	15	*2.132*	2.22	2.21	0.15	6.8	10
Cr	µg/l	A1M			3.35	15	*3.494*	3.20	3.10	0.48	15.6	11
	µg/l	D2M			1.59	15	*1.697*	1.59	1.60	0.07	4.2	6
	µg/l	N3M			3.67	15	*3.804*	3.58	3.67	0.22	5.9	9

Participant 4												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
Cu	µg/l	A1M			6.35	10	*5.906*	6.11	6.12	0.39	6.3	11
	µg/l	D2M			123	10	*124.52*	125	123	4	3.3	10
	µg/l	N3M			5.39	15	*5.06*	5.45	5.39	0.25	4.6	10
Fe	µg/l	A1M			115	10	*105.468*	116	116	7	5.9	12
	µg/l	D2M			76.9	15	*75.833*	76.9	78.2	5.6	7.1	11
	µg/l	N3M			315	15	*289.54*	317	315	23	7.2	10
Hg	µg/l	A1Hg			0.064	25	*0.07*	0.070	0.076	0.015	20.2	8
	µg/l	D2Hg			0.025	25	*0.0263*	0.027	0.027	0.003	9.5	6
	µg/l	N3Hg			0.117	20	*0.1205*	0.121	0.123	0.018	14.7	7
K	mg/l	A1M			1.50	10	*0.977*	1.53	1.52	0.02	1.3	8
	mg/l	D2M			1.42	10	*1.21*	1.41	1.42	0.04	2.5	9
	mg/l	N3M			2.21	10	*2.01*	2.21	2.21	0.03	1.1	9
Mg	mg/l	A1M			7.50	10	*6.953*	7.42	7.28	0.33	4.6	11
	mg/l	D2M			1.61	10	*1.721*	1.61	1.59	0.07	4.7	10
	mg/l	N3M			3.30	10	*3.622*	3.30	3.30	0.13	4.0	11
Mn	µg/l	A1M			9.95	10	*9.113*	9.60	9.38	0.81	8.7	12
	µg/l	D2M			11.2	15	*11.562*	11.4	11.2	0.8	7.0	11
	µg/l	N3M			6.05	15	*6.086*	6.05	6.05	0.31	5.1	11
Mo	µg/l	A1M			11.5	10	*11.402*	12.0	11.9	0.8	6.7	11
	µg/l	D2M			5.22	10	*5.053*	5.18	5.22	0.20	3.9	10
	µg/l	N3M			12.9	10	*12.619*	12.9	13.1	0.7	5.1	11
Na	mg/l	A1M			12.5	10	*10.515*	12.5	12.2	0.5	4.3	11
	mg/l	D2M			7.68	10	*7.584*	7.83	7.68	0.45	5.8	10
	mg/l	N3M			10.1	10	*9.967*	10.1	10.0	0.5	5.0	11
Ni	µg/l	A1M			2.25	10	*2.16*	2.27	2.26	0.14	6.1	8
	µg/l	D2M			2.54	15	*2.392*	2.54	2.51	0.16	6.5	8
	µg/l	N3M			6.30	10	*5.828*	6.33	6.30	0.25	3.9	9
Pb	µg/l	A1M			2.16	10	*1.718*	2.05	2.04	0.11	5.5	10
	µg/l	D2M			1.79	15	*1.518*	1.80	1.79	0.12	6.7	10
	µg/l	N3M			3.34	15	*2.763*	3.22	3.20	0.18	5.5	10
Sb	µg/l	A1M			2.25	10	*1.127*	2.26	2.26	0.10	4.3	8
	µg/l	D2M			1.03	10	*0.525*	1.02	1.03	0.04	3.8	9
	µg/l	N3M			2.00	10	*0.774*	1.99	2.00	0.08	4.0	7
Se	µg/l	A1M			1.25	15	*1.313*	1.25	1.27	0.06	4.7	8
	µg/l	D2M			2.10	15	*2.168*	2.11	2.10	0.13	6.1	10
	µg/l	N3M			5.15	10	*5.365*	5.16	5.15	0.12	2.2	9
Ti	µg/l	A1M			18.5	10	*17.373*	18.9	18.8	1.0	5.3	8
	µg/l	D2M			2.36		*2.325*	2.45	2.36	0.26	10.9	5
	µg/l	N3M			28.4	20	*20.771*	29.2	28.4	1.5	5.2	7
V	µg/l	A1M			3.35	10	*3.575*	3.34	3.31	0.18	5.5	8
	µg/l	D2M			1.56	15	*1.661*	1.58	1.56	0.07	4.7	7
	µg/l	N3M			4.83	15	*4.994*	4.92	4.83	0.24	5.0	7
Zn	µg/l	A1M			13.5	10	*13.393*	13.5	13.5	0.4	2.6	9
	µg/l	D2M			6.53	15	*6.787*	6.43	6.53	0.35	5.4	9
	µg/l	N3M			22.7	10	*22.734*	22.6	22.7	0.5	2.3	9

Participant 5												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Al	µg/l	A1M		-0.39	25.5	20	24.5	28.2	28.2	2.0	7.2	10
	µg/l	D2M		-2.04	14.7	20	11.7	14.7	14.8	1.7	11.3	11
	µg/l	N3M		-0.46	527	20	503	527	515	52	10.2	11
Ba	µg/l	A1M		-0.77	15.5	10	14.9	15.1	15.0	0.7	4.5	9
	µg/l	D2M		-0.11	5.46	10	5.43	5.53	5.46	0.26	4.8	9
	µg/l	N3M		0.84	38.0	10	39.6	38.5	38.0	1.7	4.6	9
Ca	mg/l	A1M		-2.09	17.5	10	15.7	17.1	16.9	0.8	4.6	11
	mg/l	D2M		-1.37	18.6	10	17.3	18.8	18.6	0.7	3.7	10
	mg/l	N3M		-1.33	8.69	10	8.11	8.69	8.69	0.33	3.8	11
Cd	µg/l	A1M		-0.31	0.65	10	0.64	0.66	0.65	0.03	4.5	11
	µg/l	D2M		0.61	0.22	15	0.23	0.22	0.22	0.01	6.0	10
	µg/l	N3M		0.00	0.54	15	0.54	0.54	0.54	0.02	4.3	10
Co	µg/l	A1M		1.33	1.95	10	2.08	1.93	1.94	0.09	4.8	10
	µg/l	D2M		0.58	1.61	15	1.68	1.60	1.61	0.12	7.5	8
	µg/l	N3M		0.66	2.21	15	2.32	2.22	2.21	0.15	6.8	10
Cr	µg/l	A1M		-2.95	3.35	15	2.61	3.20	3.10	0.48	15.6	11
	µg/l	D2M		-4.03	1.59	15	1.11	1.59	1.60	0.07	4.2	6
	µg/l	N3M		4.94	3.67	15	5.03	3.58	3.67	0.22	5.9	9
Cu	µg/l	A1M		8.50	6.35	10	9.05	6.11	6.12	0.39	6.3	11
	µg/l	D2M		0.16	123	10	124	125	123	4	3.3	10
	µg/l	N3M		8.34	5.39	15	8.76	5.45	5.39	0.25	4.6	10
Fe	µg/l	A1M		0.17	115	10	116	116	116	7	5.9	12
	µg/l	D2M		0.19	76.9	15	78.0	76.9	78.2	5.6	7.1	11
	µg/l	N3M		0.42	315	15	325	317	315	23	7.2	10
K	mg/l	A1M		0.00	1.50	10	1.50	1.53	1.52	0.02	1.3	8
	mg/l	D2M		-0.42	1.42	10	1.39	1.41	1.42	0.04	2.5	9
	mg/l	N3M		0.00	2.21	10	2.21	2.21	2.21	0.03	1.1	9
Mg	mg/l	A1M		-2.32	7.50	10	6.63	7.42	7.28	0.33	4.6	11
	mg/l	D2M		-1.99	1.61	10	1.45	1.61	1.59	0.07	4.7	10
	mg/l	N3M		-1.58	3.30	10	3.04	3.30	3.30	0.13	4.0	11
Mn	µg/l	A1M		-0.54	9.95	10	9.68	9.60	9.38	0.81	8.7	12
	µg/l	D2M		0.36	11.2	15	11.5	11.4	11.2	0.8	7.0	11
	µg/l	N3M		0.37	6.05	15	6.22	6.05	6.05	0.31	5.1	11
Mo	µg/l	A1M		-0.70	11.5	10	11.1	12.0	11.9	0.8	6.7	11
	µg/l	D2M		-0.84	5.22	10	5.00	5.18	5.22	0.20	3.9	10
	µg/l	N3M		-0.16	12.9	10	12.8	12.9	13.1	0.7	5.1	11
Na	mg/l	A1M		0.18	12.5	10	12.6	12.5	12.2	0.5	4.3	11
	mg/l	D2M		0.73	7.68	10	7.96	7.83	7.68	0.45	5.8	10
	mg/l	N3M		0.55	10.1	10	10.4	10.1	10.0	0.5	5.0	11
Ni	µg/l	A1M		-0.71	2.25	10	2.17	2.27	2.26	0.14	6.1	8
	µg/l	D2M		-0.68	2.54	15	2.41	2.54	2.51	0.16	6.5	8
	µg/l	N3M		-0.06	6.30	10	6.28	6.33	6.30	0.25	3.9	9
Se	µg/l	A1M		-2.99	1.25	15	0.97	1.25	1.27	0.06	4.7	8
	µg/l	D2M		-1.33	2.10	15	1.89	2.11	2.10	0.13	6.1	10
	µg/l	N3M		-0.70	5.15	10	4.97	5.16	5.15	0.12	2.2	9
Zn	µg/l	A1M		0.89	13.5	10	14.1	13.5	13.5	0.4	2.6	9
	µg/l	D2M		0.51	6.53	15	6.78	6.43	6.53	0.35	5.4	9
	µg/l	N3M		0.64	22.7	10	23.4	22.6	22.7	0.5	2.3	9

Participant 6												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Al	µg/l	A1M		0.43	25.5	20	26.6	28.2	28.2	2.0	7.2	10
	µg/l	D2M		-0.34	14.7	20	14.2	14.7	14.8	1.7	11.3	11
	µg/l	N3M		-0.30	527	20	511	527	515	52	10.2	11
As	µg/l	A1M		-0.65	2.25	15	2.14	2.14	2.11	0.11	5.4	9
	µg/l	D2M		0.00	2.16	10	2.16	2.16	2.17	0.11	5.1	9
	µg/l	N3M		0.31	0.64	10	0.65	0.64	0.62	0.03	4.7	8
B	µg/l	A1M		1.73	25.5	15	28.8	26.9	26.5	1.9	7.3	10
	µg/l	D2M		0.68	23.4	15	24.6	23.4	23.7	1.4	6.0	9
	µg/l	N3M			16.6	20	*< 20*	16.6	16.1	1.6	10.2	8
Ba	µg/l	A1M		-1.42	15.5	10	14.4	15.1	15.0	0.7	4.5	9
	µg/l	D2M		-0.51	5.46	10	5.32	5.53	5.46	0.26	4.8	9
	µg/l	N3M		-0.84	38.0	10	36.4	38.5	38.0	1.7	4.6	9
Ca	mg/l	A1M		-1.03	17.5	10	16.6	17.1	16.9	0.8	4.6	11
	mg/l	D2M		-0.32	18.6	10	18.3	18.8	18.6	0.7	3.7	10
	mg/l	N3M		0.02	8.69	10	8.70	8.69	8.69	0.33	3.8	11
Cd	µg/l	A1M		-1.23	0.65	10	0.61	0.66	0.65	0.03	4.5	11
	µg/l	D2M		-1.21	0.22	15	0.20	0.22	0.22	0.01	6.0	10
	µg/l	N3M		-0.74	0.54	15	0.51	0.54	0.54	0.02	4.3	10
Co	µg/l	A1M		-1.74	1.95	10	1.78	1.93	1.94	0.09	4.8	10
	µg/l	D2M		-1.33	1.61	15	1.45	1.60	1.61	0.12	7.5	8
	µg/l	N3M		-1.09	2.21	15	2.03	2.22	2.21	0.15	6.8	10
Cr	µg/l	A1M		-0.88	3.35	15	3.13	3.20	3.10	0.48	15.6	11
	µg/l	D2M		-0.67	1.59	15	1.51	1.59	1.60	0.07	4.2	6
	µg/l	N3M		-0.54	3.67	15	3.52	3.58	3.67	0.22	5.9	9
Cu	µg/l	A1M		-2.46	6.35	10	5.57	6.11	6.12	0.39	6.3	11
	µg/l	D2M		-0.98	123	10	117	125	123	4	3.3	10
	µg/l	N3M		-1.06	5.39	15	4.96	5.45	5.39	0.25	4.6	10
Fe	µg/l	A1M		-0.52	115	10	112	116	116	7	5.9	12
	µg/l	D2M		-0.10	76.9	15	76.3	76.9	78.2	5.6	7.1	11
	µg/l	N3M		-0.34	315	15	307	317	315	23	7.2	10
Hg	µg/l	A1Hg		-0.50	0.064	25	0.060	0.070	0.076	0.015	20.2	8
	µg/l	D2Hg		1.28	0.025	25	0.029	0.027	0.027	0.003	9.5	6
	µg/l	N3Hg		-1.28	0.117	20	0.102	0.121	0.123	0.018	14.7	7
K	mg/l	A1M		1.73	1.50	10	1.63	1.53	1.52	0.02	1.3	8
	mg/l	D2M		0.99	1.42	10	1.49	1.41	1.42	0.04	2.5	9
	mg/l	N3M		-0.27	2.21	10	2.18	2.21	2.21	0.03	1.1	9
Mg	mg/l	A1M		-1.31	7.50	10	7.01	7.42	7.28	0.33	4.6	11
	mg/l	D2M		-0.62	1.61	10	1.56	1.61	1.59	0.07	4.7	10
	mg/l	N3M		-0.61	3.30	10	3.20	3.30	3.30	0.13	4.0	11
Mn	µg/l	A1M		-1.29	9.95	10	9.31	9.60	9.38	0.81	8.7	12
	µg/l	D2M		-0.36	11.2	15	10.9	11.4	11.2	0.8	7.0	11
	µg/l	N3M		-0.29	6.05	15	5.92	6.05	6.05	0.31	5.1	11
Mo	µg/l	A1M		0.52	11.5	10	11.8	12.0	11.9	0.8	6.7	11
	µg/l	D2M		-0.50	5.22	10	5.09	5.18	5.22	0.20	3.9	10
	µg/l	N3M		-0.93	12.9	10	12.3	12.9	13.1	0.7	5.1	11

Participant 6												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
Na	mg/l	A1M		-1.60	12.5	10	11.5	12.5	12.2	0.5	4.3	11
	mg/l	D2M		-1.38	7.68	10	7.15	7.83	7.68	0.45	5.8	10
	mg/l	N3M		-1.19	10.1	10	9.5	10.1	10.0	0.5	5.0	11
Ni	µg/l	A1M		-0.62	2.25	10	2.18	2.27	2.26	0.14	6.1	8
	µg/l	D2M		-0.84	2.54	15	2.38	2.54	2.51	0.16	6.5	8
	µg/l	N3M		-1.33	6.30	10	5.88	6.33	6.30	0.25	3.9	9
Pb	µg/l	A1M		-1.85	2.16	10	1.96	2.05	2.04	0.11	5.5	10
	µg/l	D2M		-0.82	1.79	15	1.68	1.80	1.79	0.12	6.7	10
	µg/l	N3M		-0.80	3.34	15	3.14	3.22	3.20	0.18	5.5	10
Sb	µg/l	A1M		-1.07	2.25	10	2.13	2.26	2.26	0.10	4.3	8
	µg/l	D2M		-0.58	1.03	10	1.00	1.02	1.03	0.04	3.8	9
	µg/l	N3M		-0.70	2.00	10	1.93	1.99	2.00	0.08	4.0	7
Se	µg/l	A1M		-0.21	1.25	15	1.23	1.25	1.27	0.06	4.7	8
	µg/l	D2M		-0.25	2.10	15	2.06	2.11	2.10	0.13	6.1	10
	µg/l	N3M		0.04	5.15	10	5.16	5.16	5.15	0.12	2.2	9
Ti	µg/l	A1M		1.51	18.5	10	19.9	18.9	18.8	1.0	5.3	8
	µg/l	D2M			2.36		*< 10*	2.45	2.36	0.26	10.9	5
	µg/l	N3M		-0.18	28.4	20	27.9	29.2	28.4	1.5	5.2	7
V	µg/l	A1M		-1.31	3.35	10	3.13	3.34	3.31	0.18	5.5	8
	µg/l	D2M		-0.94	1.56	15	1.45	1.58	1.56	0.07	4.7	7
	µg/l	N3M		-0.94	4.83	15	4.49	4.92	4.83	0.24	5.0	7
Zn	µg/l	A1M		-0.15	13.5	10	13.4	13.5	13.5	0.4	2.6	9
	µg/l	D2M		-0.53	6.53	15	6.27	6.43	6.53	0.35	5.4	9
	µg/l	N3M		0.09	22.7	10	22.8	22.6	22.7	0.5	2.3	9

Participant 7												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
Hg	µg/l	A1Hg		4.00	0.064	25	0.096	0.070	0.076	0.015	20.2	8
	µg/l	D2Hg		3.78	0.025	25	0.037	0.027	0.027	0.003	9.5	6
	µg/l	N3Hg		3.59	0.117	20	0.159	0.121	0.123	0.018	14.7	7

Participant 9												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
Hg	µg/l	A1Hg		4.03	0.064	25	0.096	0.070	0.076	0.015	20.2	8
	µg/l	D2Hg		6.94	0.025	25	0.047	0.027	0.027	0.003	9.5	6
	µg/l	N3Hg		5.64	0.117	20	0.183	0.121	0.123	0.018	14.7	7

Participant 10												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
Al	µg/l	A1M		1.45	25.5	20	29.2	28.2	28.2	2.0	7.2	10
	µg/l	D2M		0.00	14.7	20	14.7	14.7	14.8	1.7	11.3	11
	µg/l	N3M		0.99	527	20	579	527	515	52	10.2	11
As	µg/l	A1M		-1.72	2.25	15	1.96	2.14	2.11	0.11	5.4	9
	µg/l	D2M		1.11	2.16	10	2.28	2.16	2.17	0.11	5.1	9
	µg/l	N3M		0.00	0.64	10	0.64	0.64	0.62	0.03	4.7	8
B	µg/l	A1M		0.31	25.5	15	26.1	26.9	26.5	1.9	7.3	10
	µg/l	D2M		0.00	23.4	15	23.4	23.4	23.7	1.4	6.0	9
	µg/l	N3M		0.30	16.6	20	17.1	16.6	16.1	1.6	10.2	8

Participant 10												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Ba	µg/l	A1M		-0.13	15.5	10	15.4	15.1	15.0	0.7	4.5	9
	µg/l	D2M		0.73	5.46	10	5.66	5.53	5.46	0.26	4.8	9
	µg/l	N3M		0.63	38.0	10	39.2	38.5	38.0	1.7	4.6	9
Ca	mg/l	A1M		0.00	17.5	10	17.5	17.1	16.9	0.8	4.6	11
	mg/l	D2M		0.65	18.6	10	19.2	18.8	18.6	0.7	3.7	10
	mg/l	N3M		0.55	8.69	10	8.93	8.69	8.69	0.33	3.8	11
Cd	µg/l	A1M		-0.92	0.65	10	0.62	0.66	0.65	0.03	4.5	11
	µg/l	D2M		-0.61	0.22	15	0.21	0.22	0.22	0.01	6.0	10
	µg/l	N3M		-0.25	0.54	15	0.53	0.54	0.54	0.02	4.3	10
Co	µg/l	A1M		0.10	1.95	10	1.96	1.93	1.94	0.09	4.8	10
	µg/l	D2M		0.00	1.61	15	1.61	1.60	1.61	0.12	7.5	8
	µg/l	N3M		0.18	2.21	15	2.24	2.22	2.21	0.15	6.8	10
Cr	µg/l	A1M		-0.60	3.35	15	3.20	3.20	3.10	0.48	15.6	11
	µg/l	D2M		-0.25	1.59	15	1.56	1.59	1.60	0.07	4.2	6
	µg/l	N3M		-0.33	3.67	15	3.58	3.58	3.67	0.22	5.9	9
Cu	µg/l	A1M		-0.63	6.35	10	6.15	6.11	6.12	0.39	6.3	11
	µg/l	D2M		0.33	123	10	125	125	123	4	3.3	10
	µg/l	N3M		0.32	5.39	15	5.52	5.45	5.39	0.25	4.6	10
Fe	µg/l	A1M		0.00	115	10	115	116	116	7	5.9	12
	µg/l	D2M		0.10	76.9	15	77.5	76.9	78.2	5.6	7.1	11
	µg/l	N3M		1.69	315	15	355	317	315	23	7.2	10
Hg	µg/l	A1Hg		3.13	0.064	25	0.089	0.070	0.076	0.015	20.2	8
	µg/l	D2Hg		1.28	0.025	25	0.029	0.027	0.027	0.003	9.5	6
	µg/l	N3Hg		1.11	0.117	20	0.130	0.121	0.123	0.018	14.7	7
K	mg/l	A1M		0.40	1.50	10	1.53	1.53	1.52	0.02	1.3	8
	mg/l	D2M		0.14	1.42	10	1.43	1.41	1.42	0.04	2.5	9
	mg/l	N3M		0.18	2.21	10	2.23	2.21	2.21	0.03	1.1	9
Mg	mg/l	A1M		0.21	7.50	10	7.58	7.42	7.28	0.33	4.6	11
	mg/l	D2M		0.37	1.61	10	1.64	1.61	1.59	0.07	4.7	10
	mg/l	N3M		1.09	3.30	10	3.48	3.30	3.30	0.13	4.0	11
Mn	µg/l	A1M		0.50	9.95	10	10.20	9.60	9.38	0.81	8.7	12
	µg/l	D2M		0.95	11.2	15	12.0	11.4	11.2	0.8	7.0	11
	µg/l	N3M		1.12	6.05	15	6.56	6.05	6.05	0.31	5.1	11
Mo	µg/l	A1M		1.04	11.5	10	12.1	12.0	11.9	0.8	6.7	11
	µg/l	D2M		0.88	5.22	10	5.45	5.18	5.22	0.20	3.9	10
	µg/l	N3M		1.24	12.9	10	13.7	12.9	13.1	0.7	5.1	11
Na	mg/l	A1M		0.16	12.5	10	12.6	12.5	12.2	0.5	4.3	11
	mg/l	D2M		0.55	7.68	10	7.89	7.83	7.68	0.45	5.8	10
	mg/l	N3M		0.59	10.1	10	10.4	10.1	10.0	0.5	5.0	11
Ni	µg/l	A1M		0.98	2.25	10	2.36	2.27	2.26	0.14	6.1	8
	µg/l	D2M		0.42	2.54	15	2.62	2.54	2.51	0.16	6.5	8
	µg/l	N3M		0.32	6.30	10	6.40	6.33	6.30	0.25	3.9	9
Pb	µg/l	A1M		-1.85	2.16	10	1.96	2.05	2.04	0.11	5.5	10
	µg/l	D2M		-0.52	1.79	15	1.72	1.80	1.79	0.12	6.7	10
	µg/l	N3M		-0.60	3.34	15	3.19	3.22	3.20	0.18	5.5	10
Sb	µg/l	A1M		-0.98	2.25	10	2.14	2.26	2.26	0.10	4.3	8
	µg/l	D2M		-0.19	1.03	10	1.02	1.02	1.03	0.04	3.8	9
	µg/l	N3M		0.50	2.00	10	2.05	1.99	2.00	0.08	4.0	7

Participant 10												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Se	µg/l	A1M		-0.53	1.25	15	1.20	1.25	1.27	0.06	4.7	8
	µg/l	D2M		-0.89	2.10	15	1.96	2.11	2.10	0.13	6.1	10
	µg/l	N3M		-0.08	5.15	10	5.13	5.16	5.15	0.12	2.2	9
Ti	µg/l	A1M		0.22	18.5	10	18.7	18.9	18.8	1.0	5.3	8
	µg/l	D2M			2.36		*<15*	2.45	2.36	0.26	10.9	5
	µg/l	N3M		0.32	28.4	20	29.3	29.2	28.4	1.5	5.2	7
V	µg/l	A1M		-0.66	3.35	10	3.24	3.34	3.31	0.18	5.5	8
	µg/l	D2M		-0.43	1.56	15	1.51	1.58	1.56	0.07	4.7	7
	µg/l	N3M		-0.17	4.83	15	4.77	4.92	4.83	0.24	5.0	7
Zn	µg/l	A1M		-0.15	13.5	10	13.4	13.5	13.5	0.4	2.6	9
	µg/l	D2M		-0.25	6.53	15	6.41	6.43	6.53	0.35	5.4	9
	µg/l	N3M		-0.09	22.7	10	22.6	22.6	22.7	0.5	2.3	9

Participant 11												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Al	µg/l	A1M		0.82	25.5	20	27.6	28.2	28.2	2.0	7.2	10
	µg/l	D2M		-0.30	14.7	20	14.3	14.7	14.8	1.7	11.3	11
	µg/l	N3M		-2.27	527	20	407	527	515	52	10.2	11
Cd	µg/l	A1M		0.63	0.65	10	0.67	0.66	0.65	0.03	4.5	11
	µg/l	D2M		0.48	0.22	15	0.23	0.22	0.22	0.01	6.0	10
	µg/l	N3M		0.60	0.54	15	0.56	0.54	0.54	0.02	4.3	10
Cu	µg/l	A1M		0.85	6.35	10	6.62	6.11	6.12	0.39	6.3	11
	µg/l	D2M		0.49	123	10	126	125	123	4	3.3	10
	µg/l	N3M		0.56	5.39	15	5.62	5.45	5.39	0.25	4.6	10
Fe	µg/l	A1M		1.86	115	10	126	116	116	7	5.9	12
	µg/l	D2M		1.53	76.9	15	85.7	76.9	78.2	5.6	7.1	11
	µg/l	N3M		-0.97	315	15	292	317	315	23	7.2	10
Mn	µg/l	A1M		0.00	9.95	10	9.95	9.60	9.38	0.81	8.7	12
	µg/l	D2M		0.44	11.2	15	11.6	11.4	11.2	0.8	7.0	11
	µg/l	N3M		0.00	6.05	15	6.05	6.05	6.05	0.31	5.1	11
Mo	µg/l	A1M		2.61	11.5	10	13.0	12.0	11.9	0.8	6.7	11
	µg/l	D2M		0.46	5.22	10	5.34	5.18	5.22	0.20	3.9	10
	µg/l	N3M		2.14	12.9	10	14.3	12.9	13.1	0.7	5.1	11
Pb	µg/l	A1M		-0.57	2.16	10	2.10	2.05	2.04	0.11	5.5	10
	µg/l	D2M		0.34	1.79	15	1.84	1.80	1.79	0.12	6.7	10
	µg/l	N3M		0.06	3.34	15	3.36	3.22	3.20	0.18	5.5	10
Zn	µg/l	A1M		0.27	13.5	10	13.7	13.5	13.5	0.4	2.6	9
	µg/l	D2M		0.22	6.53	15	6.64	6.43	6.53	0.35	5.4	9
	µg/l	N3M		-0.07	22.7	10	22.6	22.6	22.7	0.5	2.3	9

Participant 12												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Al	µg/l	A1M		1.53	25.5	20	29.4	28.2	28.2	2.0	7.2	10
	µg/l	D2M		0.14	14.7	20	14.9	14.7	14.8	1.7	11.3	11
	µg/l	N3M		0.23	527	20	539	527	515	52	10.2	11
As	µg/l	A1M		-0.18	2.25	15	2.22	2.14	2.11	0.11	5.4	9
	µg/l	D2M		1.20	2.16	10	2.29	2.16	2.17	0.11	5.1	9
	µg/l	N3M		0.09	0.64	10	0.64	0.64	0.62	0.03	4.7	8

Participant 12												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
B	µg/l	A1M		0.37	25.5	15	26.2	26.9	26.5	1.9	7.3	10
	µg/l	D2M		0.00	23.4	15	23.4	23.4	23.7	1.4	6.0	9
	µg/l	N3M		0.48	16.6	20	17.4	16.6	16.1	1.6	10.2	8
Ba	µg/l	A1M		0.90	15.5	10	16.2	15.1	15.0	0.7	4.5	9
	µg/l	D2M		1.21	5.46	10	5.79	5.53	5.46	0.26	4.8	9
	µg/l	N3M		1.32	38.0	10	40.5	38.5	38.0	1.7	4.6	9
Ca	mg/l	A1M		-0.46	17.5	10	17.1	17.1	16.9	0.8	4.6	11
	mg/l	D2M		-0.11	18.6	10	18.5	18.8	18.6	0.7	3.7	10
	mg/l	N3M		0.94	8.69	10	9.10	8.69	8.69	0.33	3.8	11
Cd	µg/l	A1M		1.32	0.65	10	0.69	0.66	0.65	0.03	4.5	11
	µg/l	D2M		-0.06	0.22	15	0.22	0.22	0.22	0.01	6.0	10
	µg/l	N3M		0.86	0.54	15	0.58	0.54	0.54	0.02	4.3	10
Co	µg/l	A1M		1.13	1.95	10	2.06	1.93	1.94	0.09	4.8	10
	µg/l	D2M		0.91	1.61	15	1.72	1.60	1.61	0.12	7.5	8
	µg/l	N3M		0.90	2.21	15	2.36	2.22	2.21	0.15	6.8	10
Cr	µg/l	A1M		0.72	3.35	15	3.53	3.20	3.10	0.48	15.6	11
	µg/l	D2M		1.01	1.59	15	1.71	1.59	1.60	0.07	4.2	6
	µg/l	N3M		1.05	3.67	15	3.96	3.58	3.67	0.22	5.9	9
Cu	µg/l	A1M		1.42	6.35	10	6.80	6.11	6.12	0.39	6.3	11
	µg/l	D2M		2.28	123	10	137	125	123	4	3.3	10
	µg/l	N3M		0.87	5.39	15	5.74	5.45	5.39	0.25	4.6	10
Fe	µg/l	A1M		1.57	115	10	124	116	116	7	5.9	12
	µg/l	D2M		1.51	76.9	15	85.6	76.9	78.2	5.6	7.1	11
	µg/l	N3M		0.97	315	15	338	317	315	23	7.2	10
Hg	µg/l	A1Hg		0.25	0.064	25	0.066	0.070	0.076	0.015	20.2	8
	µg/l	D2Hg		0.00	0.025	25	0.025	0.027	0.027	0.003	9.5	6
	µg/l	N3Hg		0.34	0.117	20	0.121	0.121	0.123	0.018	14.7	7
K	mg/l	A1M		0.67	1.50	10	1.55	1.53	1.52	0.02	1.3	8
	mg/l	D2M		-0.56	1.42	10	1.38	1.41	1.42	0.04	2.5	9
	mg/l	N3M		-0.27	2.21	10	2.18	2.21	2.21	0.03	1.1	9
Mg	mg/l	A1M		0.45	7.50	10	7.67	7.42	7.28	0.33	4.6	11
	mg/l	D2M		0.12	1.61	10	1.62	1.61	1.59	0.07	4.7	10
	mg/l	N3M		0.36	3.30	10	3.36	3.30	3.30	0.13	4.0	11
Mn	µg/l	A1M		0.90	9.95	10	10.40	9.60	9.38	0.81	8.7	12
	µg/l	D2M		1.19	11.2	15	12.2	11.4	11.2	0.8	7.0	11
	µg/l	N3M		0.77	6.05	15	6.40	6.05	6.05	0.31	5.1	11
Mo	µg/l	A1M		3.13	11.5	10	13.3	12.0	11.9	0.8	6.7	11
	µg/l	D2M		1.23	5.22	10	5.54	5.18	5.22	0.20	3.9	10
	µg/l	N3M		1.40	12.9	10	13.8	12.9	13.1	0.7	5.1	11
Na	mg/l	A1M		-0.96	12.5	10	11.9	12.5	12.2	0.5	4.3	11
	mg/l	D2M		-1.07	7.68	10	7.27	7.83	7.68	0.45	5.8	10
	mg/l	N3M		-1.52	10.1	10	9.3	10.1	10.0	0.5	5.0	11
Ni	µg/l	A1M		1.60	2.25	10	2.43	2.27	2.26	0.14	6.1	8
	µg/l	D2M		0.94	2.54	15	2.72	2.54	2.51	0.16	6.5	8
	µg/l	N3M		1.43	6.30	10	6.75	6.33	6.30	0.25	3.9	9
Pb	µg/l	A1M		0.37	2.16	10	2.20	2.05	2.04	0.11	5.5	10
	µg/l	D2M		0.82	1.79	15	1.90	1.80	1.79	0.12	6.7	10
	µg/l	N3M		0.60	3.34	15	3.49	3.22	3.20	0.18	5.5	10

Participant 12												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Sb	µg/l	A1M		0.44	2.25	10	2.30	2.26	2.26	0.10	4.3	8
	µg/l	D2M		0.58	1.03	10	1.06	1.02	1.03	0.04	3.8	9
	µg/l	N3M		0.80	2.00	10	2.08	1.99	2.00	0.08	4.0	7
Se	µg/l	A1M		1.39	1.25	15	1.38	1.25	1.27	0.06	4.7	8
	µg/l	D2M		1.33	2.10	15	2.31	2.11	2.10	0.13	6.1	10
	µg/l	N3M		2.49	5.15	10	5.79	5.16	5.15	0.12	2.2	9
Ti	µg/l	A1M		-1.84	18.5	10	16.8	18.9	18.8	1.0	5.3	8
	µg/l	D2M			2.36		1.25	2.45	2.36	0.26	10.9	5
	µg/l	N3M		-0.49	28.4	20	27.0	29.2	28.4	1.5	5.2	7
V	µg/l	A1M		1.37	3.35	10	3.58	3.34	3.31	0.18	5.5	8
	µg/l	D2M		0.85	1.56	15	1.66	1.58	1.56	0.07	4.7	7
	µg/l	N3M		0.77	4.83	15	5.11	4.92	4.83	0.24	5.0	7
Zn	µg/l	A1M		2.07	13.5	10	14.9	13.5	13.5	0.4	2.6	9
	µg/l	D2M		1.45	6.53	15	7.24	6.43	6.53	0.35	5.4	9
	µg/l	N3M		1.94	22.7	10	24.9	22.6	22.7	0.5	2.3	9

Participant 13												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Al	µg/l	A1M		1.22	25.5	20	28.6	28.2	28.2	2.0	7.2	10
	µg/l	D2M		1.77	14.7	20	17.3	14.7	14.8	1.7	11.3	11
	µg/l	N3M		0.00	527	20	527	527	515	52	10.2	11
As	µg/l	A1M		-0.41	2.25	15	2.18	2.14	2.11	0.11	5.4	9
	µg/l	D2M		-0.19	2.16	10	2.14	2.16	2.17	0.11	5.1	9
	µg/l	N3M		-0.19	0.64	10	0.63	0.64	0.62	0.03	4.7	8
B	µg/l	A1M		0.63	25.5	15	26.7	26.9	26.5	1.9	7.3	10
	µg/l	D2M		-0.23	23.4	15	23.0	23.4	23.7	1.4	6.0	9
	µg/l	N3M			16.6	20	<20	16.6	16.1	1.6	10.2	8
Ba	µg/l	A1M		0.00	15.5	10	15.5	15.1	15.0	0.7	4.5	9
	µg/l	D2M		0.55	5.46	10	5.61	5.53	5.46	0.26	4.8	9
	µg/l	N3M		0.42	38.0	10	38.8	38.5	38.0	1.7	4.6	9
Ca	mg/l	A1M		0.46	17.5	10	17.9	17.1	16.9	0.8	4.6	11
	mg/l	D2M		1.08	18.6	10	19.6	18.8	18.6	0.7	3.7	10
	mg/l	N3M		0.94	8.69	10	9.10	8.69	8.69	0.33	3.8	11
Cd	µg/l	A1M		-0.31	0.65	10	0.64	0.66	0.65	0.03	4.5	11
	µg/l	D2M		-0.30	0.22	15	0.22	0.22	0.22	0.01	6.0	10
	µg/l	N3M		-0.05	0.54	15	0.54	0.54	0.54	0.02	4.3	10
Co	µg/l	A1M		-1.03	1.95	10	1.85	1.93	1.94	0.09	4.8	10
	µg/l	D2M		-1.08	1.61	15	1.48	1.60	1.61	0.12	7.5	8
	µg/l	N3M		-0.30	2.21	15	2.16	2.22	2.21	0.15	6.8	10
Cr	µg/l	A1M		-0.32	3.35	15	3.27	3.20	3.10	0.48	15.6	11
	µg/l	D2M		0.08	1.59	15	1.60	1.59	1.60	0.07	4.2	6
	µg/l	N3M		0.29	3.67	15	3.75	3.58	3.67	0.22	5.9	9
Cu	µg/l	A1M		-0.76	6.35	10	6.11	6.11	6.12	0.39	6.3	11
	µg/l	D2M		-0.65	123	10	119	125	123	4	3.3	10
	µg/l	N3M		0.22	5.39	15	5.48	5.45	5.39	0.25	4.6	10
Fe	µg/l	A1M		0.35	115	10	117	116	116	7	5.9	12
	µg/l	D2M		0.00	76.9	15	76.9	76.9	78.2	5.6	7.1	11
	µg/l	N3M		0.25	315	15	321	317	315	23	7.2	10

Participant 13												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Hg	µg/l	A1Hg		7.00	0.064	25	0.120	0.070	0.076	0.015	20.2	8
	µg/l	D2Hg		11.20	0.025	25	0.060	0.027	0.027	0.003	9.5	6
	µg/l	N3Hg		-8.12	0.117	20	0.022	0.121	0.123	0.018	14.7	7
K	mg/l	A1M		0.27	1.50	10	1.52	1.53	1.52	0.02	1.3	8
	mg/l	D2M		-0.28	1.42	10	1.40	1.41	1.42	0.04	2.5	9
	mg/l	N3M		0.00	2.21	10	2.21	2.21	2.21	0.03	1.1	9
Mg	mg/l	A1M		-0.05	7.50	10	7.48	7.42	7.28	0.33	4.6	11
	mg/l	D2M		-0.12	1.61	10	1.60	1.61	1.59	0.07	4.7	10
	mg/l	N3M		0.73	3.30	10	3.42	3.30	3.30	0.13	4.0	11
Mn	µg/l	A1M		-0.64	9.95	10	9.63	9.60	9.38	0.81	8.7	12
	µg/l	D2M		0.36	11.2	15	11.5	11.4	11.2	0.8	7.0	11
	µg/l	N3M		0.31	6.05	15	6.19	6.05	6.05	0.31	5.1	11
Mo	µg/l	A1M		-0.17	11.5	10	11.4	12.0	11.9	0.8	6.7	11
	µg/l	D2M		-0.19	5.22	10	5.17	5.18	5.22	0.20	3.9	10
	µg/l	N3M		0.00	12.9	10	12.9	12.9	13.1	0.7	5.1	11
Na	mg/l	A1M		0.32	12.5	10	12.7	12.5	12.2	0.5	4.3	11
	mg/l	D2M		1.02	7.68	10	8.07	7.83	7.68	0.45	5.8	10
	mg/l	N3M		0.99	10.1	10	10.6	10.1	10.0	0.5	5.0	11
Ni	µg/l	A1M		0.18	2.25	10	2.27	2.27	2.26	0.14	6.1	8
	µg/l	D2M		-0.10	2.54	15	2.52	2.54	2.51	0.16	6.5	8
	µg/l	N3M		0.10	6.30	10	6.33	6.33	6.30	0.25	3.9	9
Pb	µg/l	A1M		-0.09	2.16	10	2.15	2.05	2.04	0.11	5.5	10
	µg/l	D2M		0.45	1.79	15	1.85	1.80	1.79	0.12	6.7	10
	µg/l	N3M		-0.20	3.34	15	3.29	3.22	3.20	0.18	5.5	10
Sb	µg/l	A1M		0.00	2.25	10	2.25	2.26	2.26	0.10	4.3	8
	µg/l	D2M		-0.99	1.03	10	0.98	1.02	1.03	0.04	3.8	9
	µg/l	N3M		-0.90	2.00	10	1.91	1.99	2.00	0.08	4.0	7
Se	µg/l	A1M		-0.32	1.25	15	1.22	1.25	1.27	0.06	4.7	8
	µg/l	D2M		0.32	2.10	15	2.15	2.11	2.10	0.13	6.1	10
	µg/l	N3M		0.43	5.15	10	5.26	5.16	5.15	0.12	2.2	9
Ti	µg/l	A1M		0.32	18.5	10	18.8	18.9	18.8	1.0	5.3	8
	µg/l	D2M			2.36		2.45	2.45	2.36	0.26	10.9	5
	µg/l	N3M		0.35	28.4	20	29.4	29.2	28.4	1.5	5.2	7
V	µg/l	A1M		0.06	3.35	10	3.36	3.34	3.31	0.18	5.5	8
	µg/l	D2M		0.34	1.56	15	1.60	1.58	1.56	0.07	4.7	7
	µg/l	N3M		0.61	4.83	15	5.05	4.92	4.83	0.24	5.0	7
Zn	µg/l	A1M		0.00	13.5	10	13.5	13.5	13.5	0.4	2.6	9
	µg/l	D2M		-0.20	6.53	15	6.43	6.43	6.53	0.35	5.4	9
	µg/l	N3M		-0.18	22.7	10	22.5	22.6	22.7	0.5	2.3	9

Participant 14												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Al	µg/l	A1M		0.59	25.5	20	27.0	28.2	28.2	2.0	7.2	10
	µg/l	N3M		0.57	527	20	557	527	515	52	10.2	11
B	µg/l	A1M		-1.10	25.5	15	23.4	26.9	26.5	1.9	7.3	10
	µg/l	N3M		-1.27	16.6	20	14.5	16.6	16.1	1.6	10.2	8
Ca	mg/l	A1M		-0.34	17.5	10	17.2	17.1	16.9	0.8	4.6	11
	mg/l	N3M		0.00	8.69	10	8.69	8.69	8.69	0.33	3.8	11

Participant 14												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
Cd	µg/l	A1M		1.54	0.65	10	0.70	0.66	0.65	0.03	4.5	11
	µg/l	N3M			0.54	15	*<0.7*	0.54	0.54	0.02	4.3	10
Co	µg/l	A1M		-0.51	1.95	10	1.90	1.93	1.94	0.09	4.8	10
	µg/l	N3M		-0.66	2.21	15	2.10	2.22	2.21	0.15	6.8	10
Cr	µg/l	A1M		-1.79	3.35	15	2.90	3.20	3.10	0.48	15.6	11
	µg/l	N3M		-0.98	3.67	15	3.40	3.58	3.67	0.22	5.9	9
Cu	µg/l	A1M		-1.10	6.35	10	6.00	6.11	6.12	0.39	6.3	11
	µg/l	N3M		0.02	5.39	15	5.40	5.45	5.39	0.25	4.6	10
Fe	µg/l	A1M		-1.63	115	10	106	116	116	7	5.9	12
	µg/l	N3M		-0.33	315	15	307	317	315	23	7.2	10
K	mg/l	A1M		-0.13	1.50	10	1.49	1.53	1.52	0.02	1.3	8
	mg/l	N3M		0.36	2.21	10	2.25	2.21	2.21	0.03	1.1	9
Mg	mg/l	A1M		-0.67	7.50	10	7.25	7.42	7.28	0.33	4.6	11
	mg/l	N3M		-0.12	3.30	10	3.28	3.30	3.30	0.13	4.0	11
Mn	µg/l	A1M		-2.11	9.95	10	8.90	9.60	9.38	0.81	8.7	12
	µg/l	N3M		-0.77	6.05	15	5.70	6.05	6.05	0.31	5.1	11
Mo	µg/l	A1M		-1.57	11.5	10	10.6	12.0	11.9	0.8	6.7	11
	µg/l	N3M		-0.93	12.9	10	12.3	12.9	13.1	0.7	5.1	11
Na	mg/l	A1M		-0.42	12.5	10	12.2	12.5	12.2	0.5	4.3	11
	mg/l	N3M		0.00	10.1	10	10.1	10.1	10.0	0.5	5.0	11
Ni	µg/l	A1M			2.25	10	*<2*	2.27	2.26	0.14	6.1	8
	µg/l	N3M		0.32	6.30	10	6.40	6.33	6.30	0.25	3.9	9
Pb	µg/l	A1M			2.16	10	*<5*	2.05	2.04	0.11	5.5	10
	µg/l	N3M			3.34	15	*<5*	3.22	3.20	0.18	5.5	10
Zn	µg/l	A1M		-0.59	13.5	10	13.1	13.5	13.5	0.4	2.6	9
	µg/l	N3M		-0.62	22.7	10	22.0	22.6	22.7	0.5	2.3	9

Participant 15												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
Al	µg/l	A1M		-2.31	25.5	20	19.6	28.2	28.2	2.0	7.2	10
	µg/l	D2M		-1.16	14.7	20	13.0	14.7	14.8	1.7	11.3	11
	µg/l	N3M		-1.84	527	20	430	527	515	52	10.2	11
As	µg/l	A1M		-1.78	2.25	15	1.95	2.14	2.11	0.11	5.4	9
	µg/l	D2M		-1.11	2.16	10	2.04	2.16	2.17	0.11	5.1	9
	µg/l	N3M		-2.19	0.64	10	0.57	0.64	0.62	0.03	4.7	8
B	µg/l	A1M		1.83	25.5	15	29.0	26.9	26.5	1.9	7.3	10
	µg/l	D2M		0.91	23.4	15	25.0	23.4	23.7	1.4	6.0	9
	µg/l	N3M		-1.57	16.6	20	14.0	16.6	16.1	1.6	10.2	8
Ca	mg/l	A1M		-1.49	17.5	10	16.2	17.1	16.9	0.8	4.6	11
	mg/l	D2M		-0.86	18.6	10	17.8	18.8	18.6	0.7	3.7	10
	mg/l	N3M		-0.78	8.69	10	8.35	8.69	8.69	0.33	3.8	11
Cd	µg/l	A1M		-0.62	0.65	10	0.63	0.66	0.65	0.03	4.5	11
	µg/l	D2M		-0.61	0.22	15	0.21	0.22	0.22	0.01	6.0	10
	µg/l	N3M		-0.49	0.54	15	0.52	0.54	0.54	0.02	4.3	10
Cr	µg/l	A1M		-4.22	3.35	15	2.29	3.20	3.10	0.48	15.6	11
	µg/l	D2M		-7.04	1.59	15	0.75	1.59	1.60	0.07	4.2	6
	µg/l	N3M		-4.00	3.67	15	2.57	3.58	3.67	0.22	5.9	9

Participant 15												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Cu	µg/l	A1M		-2.68	6.35	10	5.50	6.11	6.12	0.39	6.3	11
	µg/l	D2M		-1.30	123	10	115	125	123	4	3.3	10
	µg/l	N3M		0.27	5.39	15	5.50	5.45	5.39	0.25	4.6	10
Fe	µg/l	A1M		-1.74	115	10	105	116	116	7	5.9	12
	µg/l	D2M		-1.13	76.9	15	70.4	76.9	78.2	5.6	7.1	11
	µg/l	N3M		-1.74	315	15	274	317	315	23	7.2	10
Hg	µg/l	A1Hg		1.25	0.064	25	0.074	0.070	0.076	0.015	20.2	8
	µg/l	D2Hg		1.28	0.025	25	0.029	0.027	0.027	0.003	9.5	6
	µg/l	N3Hg		0.34	0.117	20	0.121	0.121	0.123	0.018	14.7	7
Mg	mg/l	A1M		-1.84	7.50	10	6.81	7.42	7.28	0.33	4.6	11
	mg/l	D2M		-1.61	1.61	10	1.48	1.61	1.59	0.07	4.7	10
	mg/l	N3M		-0.91	3.30	10	3.15	3.30	3.30	0.13	4.0	11
Mn	µg/l	A1M		-2.99	9.95	10	8.46	9.60	9.38	0.81	8.7	12
	µg/l	D2M		-0.95	11.2	15	10.4	11.4	11.2	0.8	7.0	11
	µg/l	N3M		-1.28	6.05	15	5.47	6.05	6.05	0.31	5.1	11
Na	mg/l	A1M		-1.76	12.5	10	11.4	12.5	12.2	0.5	4.3	11
	mg/l	D2M		-1.43	7.68	10	7.13	7.83	7.68	0.45	5.8	10
	mg/l	N3M		-1.29	10.1	10	9.5	10.1	10.0	0.5	5.0	11
Ni	µg/l	A1M		-2.84	2.25	10	1.93	2.27	2.26	0.14	6.1	8
	µg/l	D2M		-1.63	2.54	15	2.23	2.54	2.51	0.16	6.5	8
	µg/l	N3M		-3.24	6.30	10	5.28	6.33	6.30	0.25	3.9	9
Pb	µg/l	A1M		-3.24	2.16	10	1.81	2.05	2.04	0.11	5.5	10
	µg/l	D2M		-1.56	1.79	15	1.58	1.80	1.79	0.12	6.7	10
	µg/l	N3M		-1.76	3.34	15	2.90	3.22	3.20	0.18	5.5	10
Sb	µg/l	A1M		-0.09	2.25	10	2.24	2.26	2.26	0.10	4.3	8
	µg/l	D2M		0.39	1.03	10	1.05	1.02	1.03	0.04	3.8	9
	µg/l	N3M		-0.50	2.00	10	1.95	1.99	2.00	0.08	4.0	7
Se	µg/l	A1M		0.00	1.25	15	1.25	1.25	1.27	0.06	4.7	8
	µg/l	D2M		0.13	2.10	15	2.12	2.11	2.10	0.13	6.1	10
	µg/l	N3M		-0.27	5.15	10	5.08	5.16	5.15	0.12	2.2	9

Participant 16												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Al	µg/l	A1M		4.55	25.5	20	37.1	28.2	28.2	2.0	7.2	10
	µg/l	D2M		1.90	14.7	20	17.5	14.7	14.8	1.7	11.3	11
	µg/l	N3M		-0.08	527	20	523	527	515	52	10.2	11
As	µg/l	A1M		-0.89	2.25	15	2.10	2.14	2.11	0.11	5.4	9
	µg/l	D2M		-0.56	2.16	10	2.10	2.16	2.17	0.11	5.1	9
	µg/l	N3M		-1.25	0.64	10	0.60	0.64	0.62	0.03	4.7	8
B	µg/l	A1M		1.10	25.5	15	27.6	26.9	26.5	1.9	7.3	10
	µg/l	D2M		0.00	23.4	15	23.4	23.4	23.7	1.4	6.0	9
	µg/l	N3M		0.36	16.6	20	17.2	16.6	16.1	1.6	10.2	8
Ba	µg/l	A1M		-1.42	15.5	10	14.4	15.1	15.0	0.7	4.5	9
	µg/l	D2M		-1.17	5.46	10	5.14	5.53	5.46	0.26	4.8	9
	µg/l	N3M		-1.26	38.0	10	35.6	38.5	38.0	1.7	4.6	9
Ca	mg/l	A1M		-2.29	17.5	10	15.5	17.1	16.9	0.8	4.6	11
	mg/l	D2M		0.32	18.6	10	18.9	18.8	18.6	0.7	3.7	10
	mg/l	N3M		-0.90	8.69	10	8.30	8.69	8.69	0.33	3.8	11

Participant 16												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Cd	µg/l	A1M		0.31	0.65	10	0.66	0.66	0.65	0.03	4.5	11
	µg/l	D2M		0.61	0.22	15	0.23	0.22	0.22	0.01	6.0	10
	µg/l	N3M		-0.25	0.54	15	0.53	0.54	0.54	0.02	4.3	10
Co	µg/l	A1M		-0.82	1.95	10	1.87	1.93	1.94	0.09	4.8	10
	µg/l	D2M		1.66	1.61	15	1.81	1.60	1.61	0.12	7.5	8
	µg/l	N3M		1.69	2.21	15	2.49	2.22	2.21	0.15	6.8	10
Cr	µg/l	A1M		-3.10	3.35	15	2.57	3.20	3.10	0.48	15.6	11
	µg/l	D2M		-2.68	1.59	15	1.27	1.59	1.60	0.07	4.2	6
	µg/l	N3M		-0.47	3.67	15	3.54	3.58	3.67	0.22	5.9	9
Cu	µg/l	A1M		-0.50	6.35	10	6.19	6.11	6.12	0.39	6.3	11
	µg/l	D2M		0.33	123	10	125	125	123	4	3.3	10
	µg/l	N3M		3.93	5.39	15	6.98	5.45	5.39	0.25	4.6	10
Fe	µg/l	A1M		1.74	115	10	125	116	116	7	5.9	12
	µg/l	D2M		1.80	76.9	15	87.3	76.9	78.2	5.6	7.1	11
	µg/l	N3M		2.96	315	15	385	317	315	23	7.2	10
K	mg/l	A1M		0.40	1.50	10	1.53	1.53	1.52	0.02	1.3	8
	mg/l	D2M		-0.14	1.42	10	1.41	1.41	1.42	0.04	2.5	9
	mg/l	N3M		-1.00	2.21	10	2.10	2.21	2.21	0.03	1.1	9
Mg	mg/l	A1M		0.03	7.50	10	7.51	7.42	7.28	0.33	4.6	11
	mg/l	D2M		0.75	1.61	10	1.67	1.61	1.59	0.07	4.7	10
	mg/l	N3M		0.00	3.30	10	3.30	3.30	3.30	0.13	4.0	11
Mn	µg/l	A1M		-4.92	9.95	10	7.50	9.60	9.38	0.81	8.7	12
	µg/l	D2M		-2.18	11.2	15	9.4	11.4	11.2	0.8	7.0	11
	µg/l	N3M		-4.91	6.05	15	3.82	6.05	6.05	0.31	5.1	11
Mo	µg/l	A1M		1.04	11.5	10	12.1	12.0	11.9	0.8	6.7	11
	µg/l	D2M		-0.15	5.22	10	5.18	5.18	5.22	0.20	3.9	10
	µg/l	N3M		-0.16	12.9	10	12.8	12.9	13.1	0.7	5.1	11
Na	mg/l	A1M		0.32	12.5	10	12.7	12.5	12.2	0.5	4.3	11
	mg/l	D2M		1.88	7.68	10	8.40	7.83	7.68	0.45	5.8	10
	mg/l	N3M		0.20	10.1	10	10.2	10.1	10.0	0.5	5.0	11
Ni	µg/l	A1M		-7.73	2.25	10	1.38	2.27	2.26	0.14	6.1	8
	µg/l	D2M		-5.14	2.54	15	1.56	2.54	2.51	0.16	6.5	8
	µg/l	N3M		-2.89	6.30	10	5.39	6.33	6.30	0.25	3.9	9
Pb	µg/l	A1M		-1.39	2.16	10	2.01	2.05	2.04	0.11	5.5	10
	µg/l	D2M		-0.60	1.79	15	1.71	1.80	1.79	0.12	6.7	10
	µg/l	N3M		-1.08	3.34	15	3.07	3.22	3.20	0.18	5.5	10
Sb	µg/l	A1M		0.09	2.25	10	2.26	2.26	2.26	0.10	4.3	8
	µg/l	D2M		-0.19	1.03	10	1.02	1.02	1.03	0.04	3.8	9
	µg/l	N3M		-0.10	2.00	10	1.99	1.99	2.00	0.08	4.0	7
Se	µg/l	A1M		-0.11	1.25	15	1.24	1.25	1.27	0.06	4.7	8
	µg/l	D2M		1.02	2.10	15	2.26	2.11	2.10	0.13	6.1	10
	µg/l	N3M		0.35	5.15	10	5.24	5.16	5.15	0.12	2.2	9
Ti	µg/l	A1M		0.76	18.5	10	19.2	18.9	18.8	1.0	5.3	8
	µg/l	D2M			2.36		2.67	2.45	2.36	0.26	10.9	5
	µg/l	N3M		0.56	28.4	20	30.0	29.2	28.4	1.5	5.2	7
V	µg/l	A1M		0.36	3.35	10	3.41	3.34	3.31	0.18	5.5	8
	µg/l	D2M		0.51	1.56	15	1.62	1.58	1.56	0.07	4.7	7
	µg/l	N3M		0.25	4.83	15	4.92	4.92	4.83	0.24	5.0	7

Participant 16												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
Zn	µg/l	A1M		2.37	13.5	10	15.1	13.5	13.5	0.4	2.6	9
	µg/l	D2M		21.17	6.53	15	16.90	6.43	6.53	0.35	5.4	9
	µg/l	N3M		1.94	22.7	10	24.9	22.6	22.7	0.5	2.3	9

Appendix 8. Summaries of the z and E_n scores

z scores

Measurand	Sample	1	2	3	4	5	6	7	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	%
Al	A1M	S	S	Q	.	S	S	.	.	S	S	S	S	S	q	U	.	.	.	.	.	.	.	75.0
	D2M	S	S	S	.	q	S	.	.	S	S	S	S	.	S	S	.	.	.	.	.	.	.	90.9
	N3M	u	S	S	.	S	S	.	.	S	q	S	S	S	S	S	.	.	.	.	.	.	.	83.3
As	A1M	S	S	S	.	.	S	.	.	S	.	S	S	.	S	S	.	.	.	.	.	.	.	100
	D2M	S	S	S	.	.	S	.	.	S	.	S	S	.	S	S	.	.	.	.	.	.	.	100
	N3M	S	S	U	.	.	S	.	.	S	.	S	S	.	q	S	.	.	.	.	.	.	.	77.8
B	A1M	S	S	S	.	.	S	.	.	S	.	S	S	S	S	S	.	.	.	.	.	.	.	100
	D2M	S	S	S	.	.	S	.	.	S	.	S	S	.	S	S	.	.	.	.	.	.	.	100
	N3M	S	S	S	.	.	.	.	.	S	.	S	.	S	S	S	.	.	.	.	.	.	.	100
Ba	A1M	S	S	S	.	S	S	.	.	S	.	S	S	.	.	S	.	.	.	.	.	.	.	100
	D2M	S	S	S	.	S	S	.	.	S	.	S	S	.	.	S	.	.	.	.	.	.	.	100
	N3M	S	S	S	.	S	S	.	.	S	.	S	S	.	.	S	.	.	.	.	.	.	.	100
Ca	A1M	S	S	S	.	q	S	.	.	S	.	S	S	S	S	q	.	.	.	.	.	.	.	81.8
	D2M	S	S	S	.	S	S	.	.	S	.	S	S	.	S	S	.	.	.	.	.	.	.	100
	N3M	S	S	S	.	S	S	.	.	S	.	S	S	S	S	S	.	.	.	.	.	.	.	100
Cd	A1M	S	S	U	.	S	S	.	.	S	S	S	S	S	S	S	.	.	.	.	.	.	.	91.7
	D2M	S	S	u	.	S	S	.	.	S	S	S	S	.	S	S	.	.	.	.	.	.	.	90.9
	N3M	S	S	U	.	S	S	.	.	S	S	S	S	.	S	S	.	.	.	.	.	.	.	90.9
Co	A1M	S	S	S	.	S	S	.	.	S	.	S	S	S	.	S	.	.	.	.	.	.	.	100
	D2M	S	S	u	.	S	S	.	.	S	.	S	S	.	.	S	.	.	.	.	.	.	.	88.9
	N3M	S	S	S	.	S	S	.	.	S	.	S	S	S	.	S	.	.	.	.	.	.	.	100
Cr	A1M	S	S	Q	.	q	S	.	.	S	.	S	S	S	u	u	.	.	.	.	.	.	.	63.6
	D2M	S	S	U	.	u	S	.	.	S	.	S	S	.	u	q	.	.	.	.	.	.	.	60.0
	N3M	S	S	S	.	U	S	.	.	S	.	S	S	S	u	S	.	.	.	.	.	.	.	81.8
Cu	A1M	S	S	S	.	U	q	.	.	S	S	S	S	S	q	S	.	.	.	.	.	.	.	75.0
	D2M	S	S	S	.	S	S	.	.	S	S	Q	S	.	S	S	.	.	.	.	.	.	.	90.9
	N3M	S	S	S	.	U	S	.	.	S	S	S	S	S	S	U	.	.	.	.	.	.	.	83.3
Fe	A1M	S	S	S	.	S	S	.	.	S	S	S	S	S	S	S	.	.	.	.	.	.	.	100
	D2M	S	S	S	.	S	S	.	.	S	S	S	S	.	S	S	.	.	.	.	.	.	.	100
	N3M	u	S	S	.	S	S	.	.	S	S	S	S	S	S	Q	.	.	.	.	.	.	.	83.3
Hg	A1Hg	S	S	.	.	.	S	U	U	U	.	S	U	.	S	.	.	.	.	.	.	.	.	55.6
	D2Hg	S	S	.	.	.	S	U	U	S	.	S	U	.	S	.	.	.	.	.	.	.	.	66.7
	N3Hg	S	S	.	.	.	S	U	U	S	.	S	u	.	S	.	.	.	.	.	.	.	.	66.7
K	A1M	S	S	S	.	S	S	.	.	S	.	S	S	S	.	S	.	.	.	.	.	.	.	100
	D2M	S	S	S	.	S	S	.	.	S	.	S	S	.	.	S	.	.	.	.	.	.	.	100
	N3M	S	S	S	.	S	S	.	.	S	.	S	S	S	.	S	.	.	.	.	.	.	.	100
Mg	A1M	S	S	S	.	q	S	.	.	S	.	S	S	S	S	S	.	.	.	.	.	.	.	90.9
	D2M	S	S	S	.	S	S	.	.	S	.	S	S	.	S	S	.	.	.	.	.	.	.	100
	N3M	S	S	S	.	S	S	.	.	S	.	S	S	S	S	S	.	.	.	.	.	.	.	100
Mn	A1M	S	S	S	.	S	S	.	.	S	S	S	S	q	q	u	.	.	.	.	.	.	.	75.0
	D2M	S	S	S	.	S	S	.	.	S	S	S	S	.	S	q	.	.	.	.	.	.	.	90.9
	N3M	S	S	S	.	S	S	.	.	S	S	S	S	S	S	u	.	.	.	.	.	.	.	91.7
Mo	A1M	S	S	S	.	S	S	.	.	S	Q	U	S	S	.	S	.	.	.	.	.	.	.	81.8
	D2M	S	S	S	.	S	S	.	.	S	S	S	S	.	.	S	.	.	.	.	.	.	.	100
	N3M	S	S	S	.	S	S	.	.	S	Q	S	S	S	.	S	.	.	.	.	.	.	.	90.9

Measurand	Sample	1	2	3	4	5	6	7	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	%
Na	A1M	**S**	**S**	*S*	.	*S*	**S**	.	.	**S**	.	**S**	**S**	**S**	**S**	*S*	.	.	.	.	.	.	.	100
	D2M	**S**	**S**	*S*	.	*S*	**S**	.	.	**S**	.	**S**	**S**	.	**S**	*S*	.	.	.	.	.	.	.	100
	N3M	**S**	**S**	*S*	.	*S*	**S**	.	.	**S**	.	**S**	**S**	**S**	**S**	*S*	.	.	.	.	.	.	.	100
Ni	A1M	**S**	**S**	*q*	.	*S*	**S**	.	.	**S**	.	**S**	**S**	.	**q**	*u*	.	.	.	.	.	.	.	70.0
	D2M	**S**	**S**	*Q*	.	*S*	**S**	.	.	**S**	.	**S**	**S**	.	**S**	*u*	.	.	.	.	.	.	.	80.0
	N3M	**S**	**S**	*S*	.	*S*	**S**	.	.	**S**	.	**S**	**S**	**S**	**u**	*q*	.	.	.	.	.	.	.	81.8
Pb	A1M	**S**	**S**	*S*	.	.	**S**	.	.	**S**	**S**	**S**	**S**	.	**u**	*S*	.	.	.	.	.	.	.	90.0
	D2M	**S**	**S**	*S*	.	.	**S**	.	.	**S**	**S**	**S**	**S**	.	**S**	*S*	.	.	.	.	.	.	.	100
	N3M	**S**	**S**	*S*	.	.	**S**	.	.	**S**	**S**	**S**	**S**	.	**S**	*S*	.	.	.	.	.	.	.	100
Sb	A1M	**S**	**S**	*u*	.	.	**S**	.	.	**S**	.	**S**	**S**	.	**S**	*S*	.	.	.	.	.	.	.	88.9
	D2M	**S**	**S**	*S*	.	.	**S**	.	.	**S**	.	**S**	**S**	.	**S**	*S*	.	.	.	.	.	.	.	100
	N3M	**u**	**S**	*u*	.	.	**S**	.	.	**S**	.	**S**	**S**	.	**S**	*S*	.	.	.	.	.	.	.	77.8
Se	A1M	**S**	**S**	*q*	.	*q*	**S**	.	.	**S**	.	**S**	**S**	.	**S**	*S*	.	.	.	.	.	.	.	80.0
	D2M	**S**	**S**	*S*	.	*S*	**S**	.	.	**S**	.	**S**	**S**	.	**S**	*S*	.	.	.	.	.	.	.	100
	N3M	**S**	**S**	*S*	.	*S*	**S**	.	.	**S**	.	**Q**	**S**	.	**S**	*S*	.	.	.	.	.	.	.	90.0
Ti	A1M	*S*	**S**	*S*	.	.	*S*	.	.	*S*	.	*S*	**S**	.	.	*S*	.	.	.	.	.	.	.	100
	N3M	*q*	**S**	*S*	.	.	*S*	.	.	*S*	.	*S*	**S**	.	.	*S*	.	.	.	.	.	.	.	87.5
V	A1M	**S**	**S**	*q*	.	.	**S**	.	.	**S**	.	**S**	**S**	.	.	*S*	.	.	.	.	.	.	.	87.5
	D2M	**S**	**S**	*U*	.	.	**S**	.	.	**S**	.	**S**	**S**	.	.	*S*	.	.	.	.	.	.	.	87.5
	N3M	**S**	**S**	*U*	.	.	**S**	.	.	**S**	.	**S**	**S**	.	.	*S*	.	.	.	.	.	.	.	87.5
Zn	A1M	**S**	**S**	*S*	.	*S*	**S**	.	.	**S**	**S**	**Q**	**S**	**S**	.	*Q*	.	.	.	.	.	.	.	81.8
	D2M	**S**	**S**	*S*	.	*S*	**S**	.	.	**S**	**S**	**S**	**S**	.	.	*U*	.	.	.	.	.	.	.	90.0
	N3M	**S**	**S**	*S*	.	*S*	**S**	.	.	**S**	**S**	**S**	**S**	**S**	.	*S*	.	.	.	.	.	.	.	100
%		94	100	75		81	99	0	0	99	88	94	96	96	79	78								
accredited		66	68				60	3	3	66	22	66	67	23	48									

S - satisfactory ($-2 \leq z \leq 2$), Q - questionable ($2 < z < 3$), q - questionable ($-3 < z < -2$),
U - unsatisfactory ($z \geq 3$), and u - unsatisfactory ($z \leq -3$), respectively
bold - accredited, italics - non-accredited, normal - unknown
% - percentage of satisfactory results

Totally satisfactory, % in all: 90 % in accredited: 94 % in non-accredited: 79

E_n scores

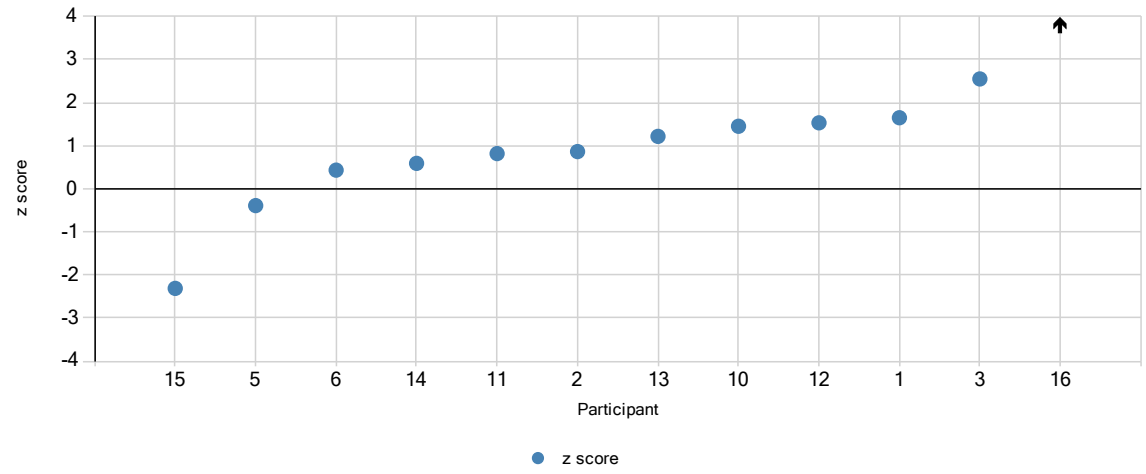
Meaurand	Sample	1	2	12	13	16	%
Ti	D2M	0.2	-0.3	-2.0	0.2	0.9	80.0
%		100	100	0	100	100	

$-1.0 \leq E_n \leq 1.0$ - satisfactory
$E_n > 1.0$ tai $E_n < -1.0$ - questionable
% - percentage of satisfactory results

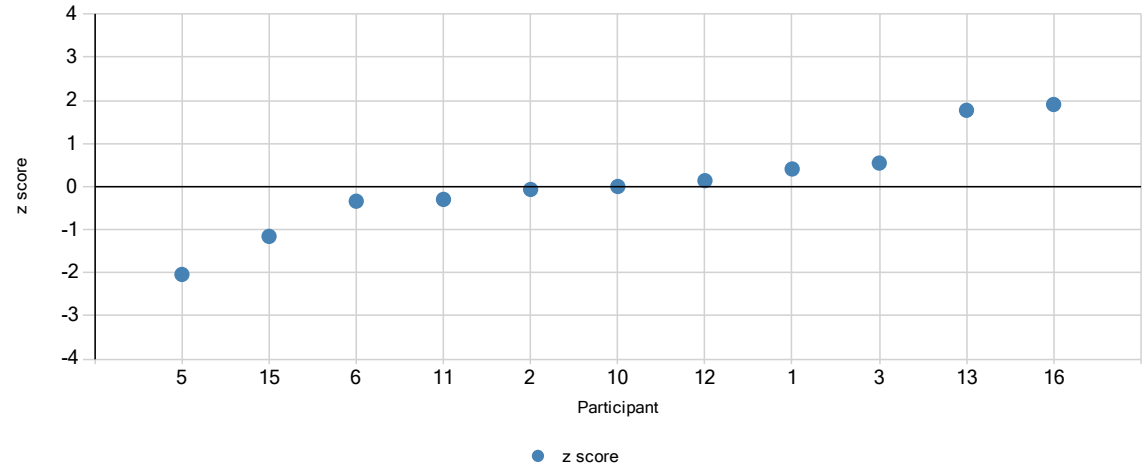
Totally satisfactory, % in all: 80

Appendix 9. z scores in ascending order

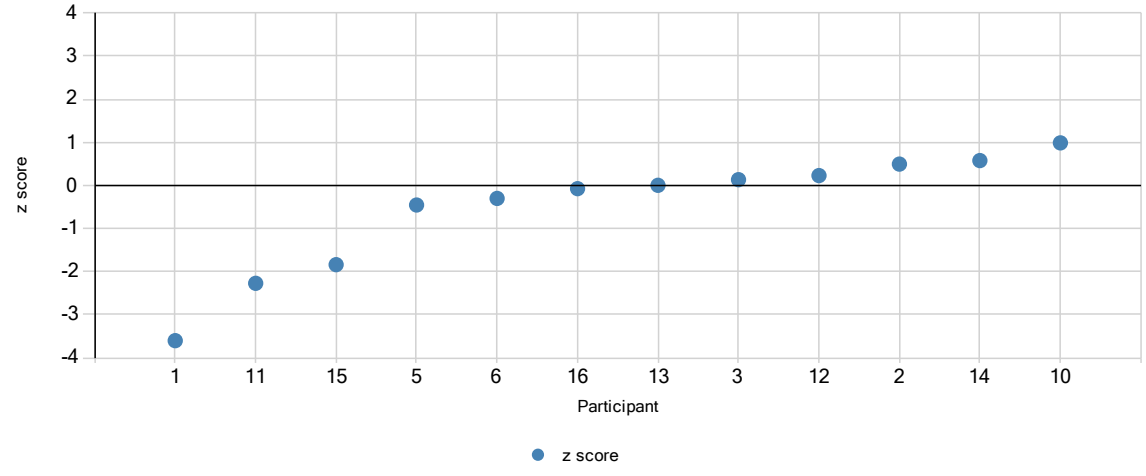
Measurand Al Sample A1M



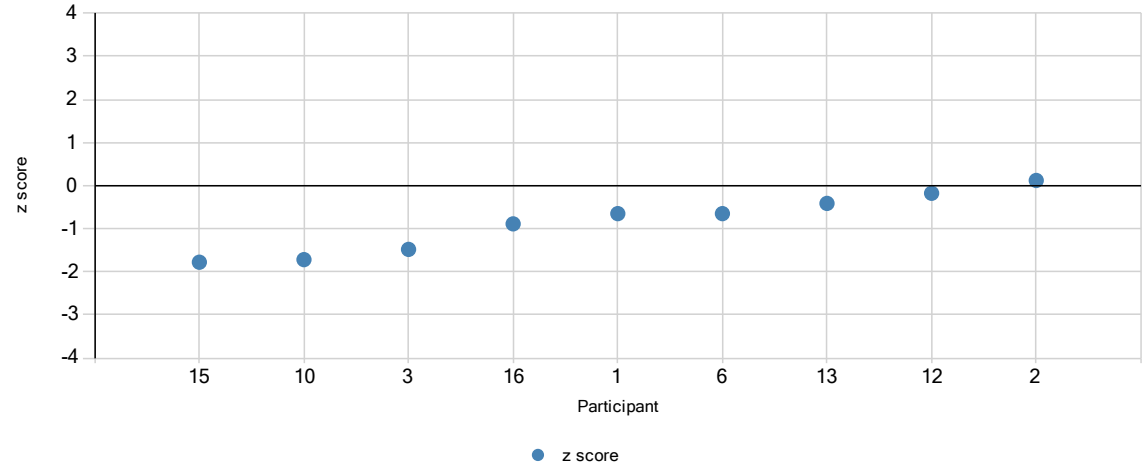
Measurand Al Sample D2M



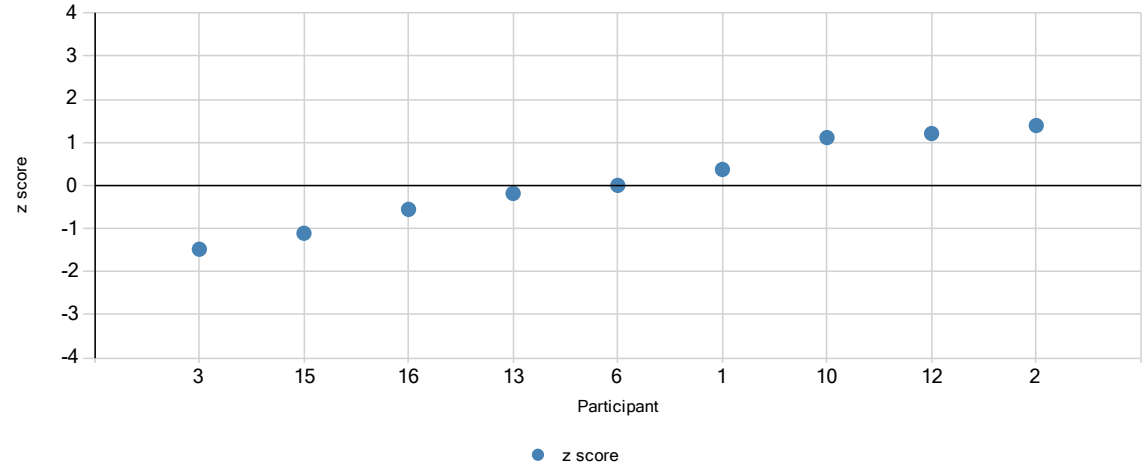
Measurand Al Sample N3M



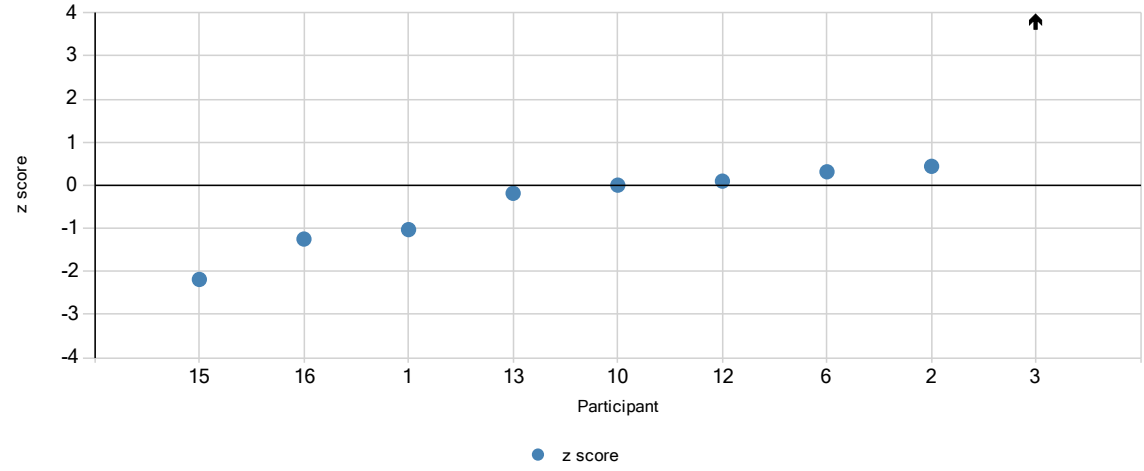
Measurand As Sample A1M



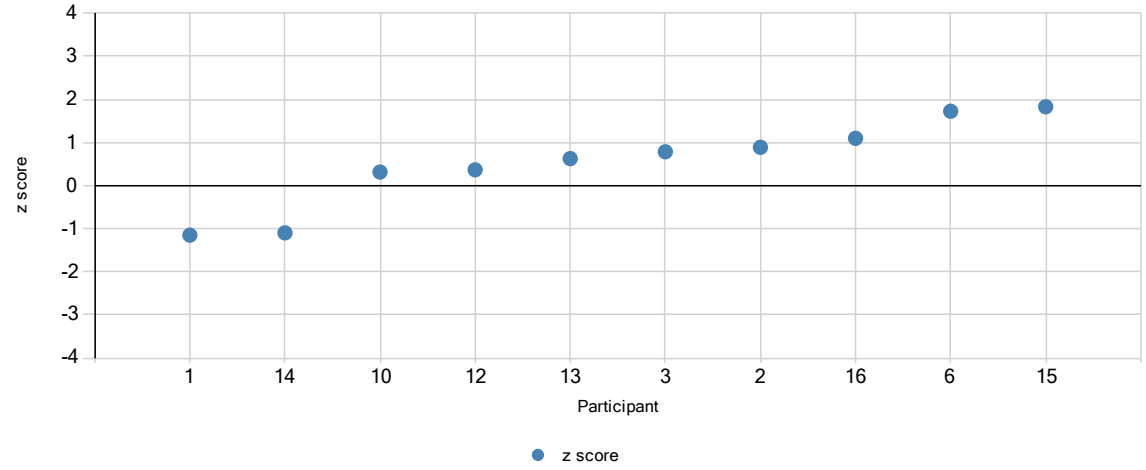
Measurand As Sample D2M



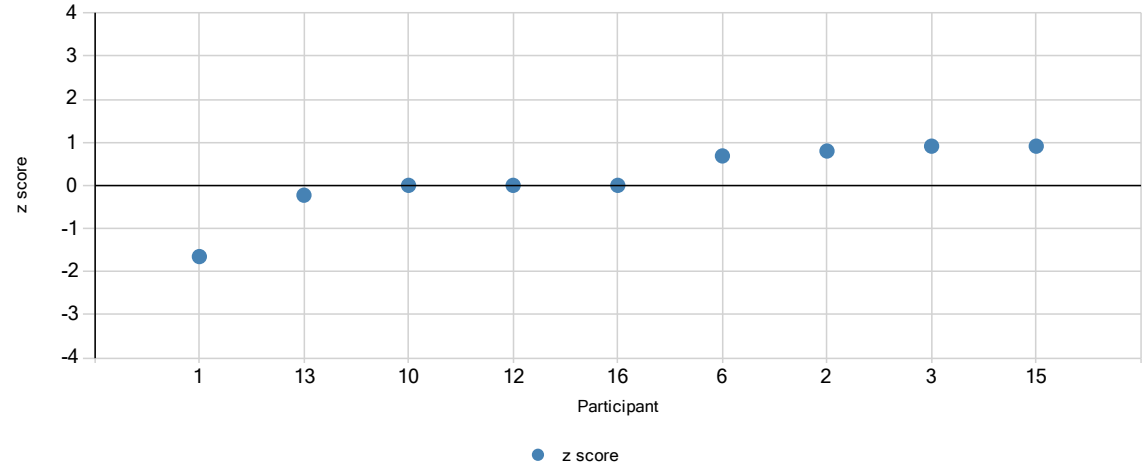
Measurand As Sample N3M



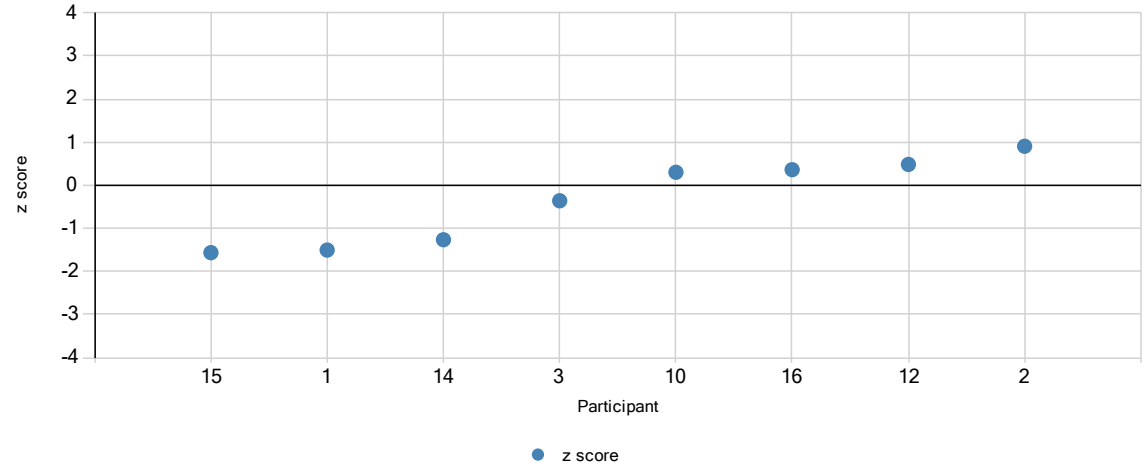
Measurand B Sample A1M

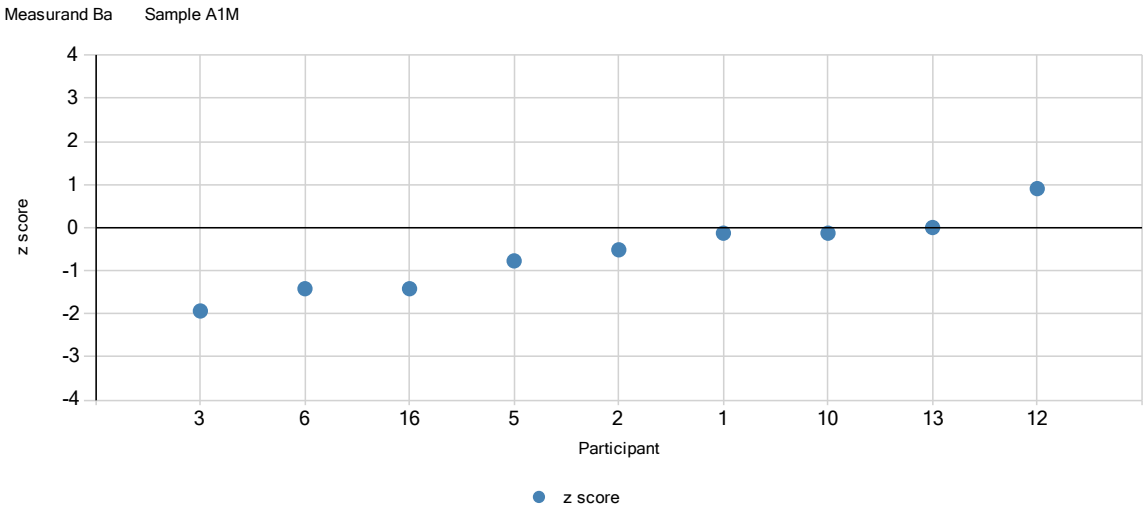


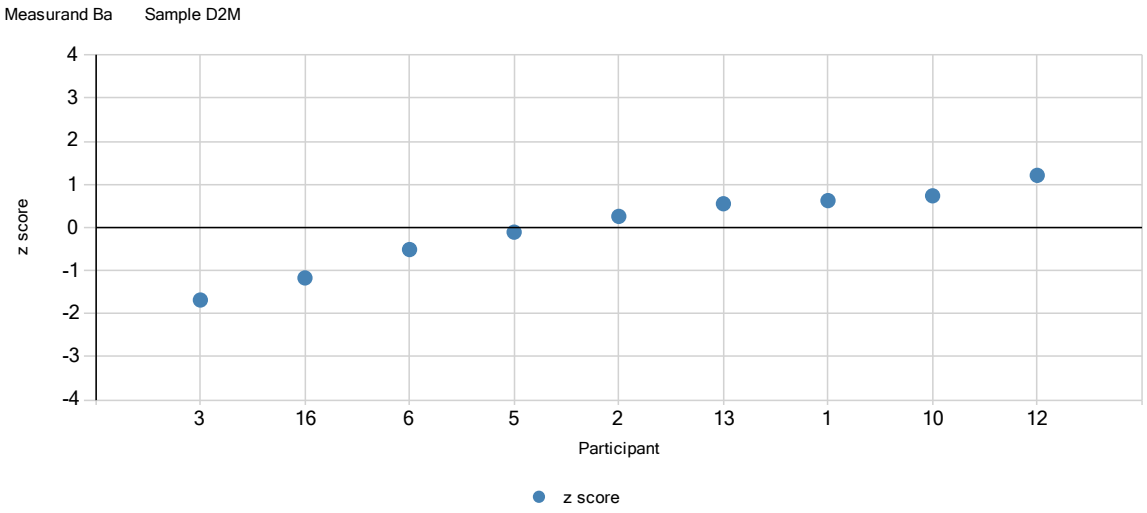
Measurand B Sample D2M

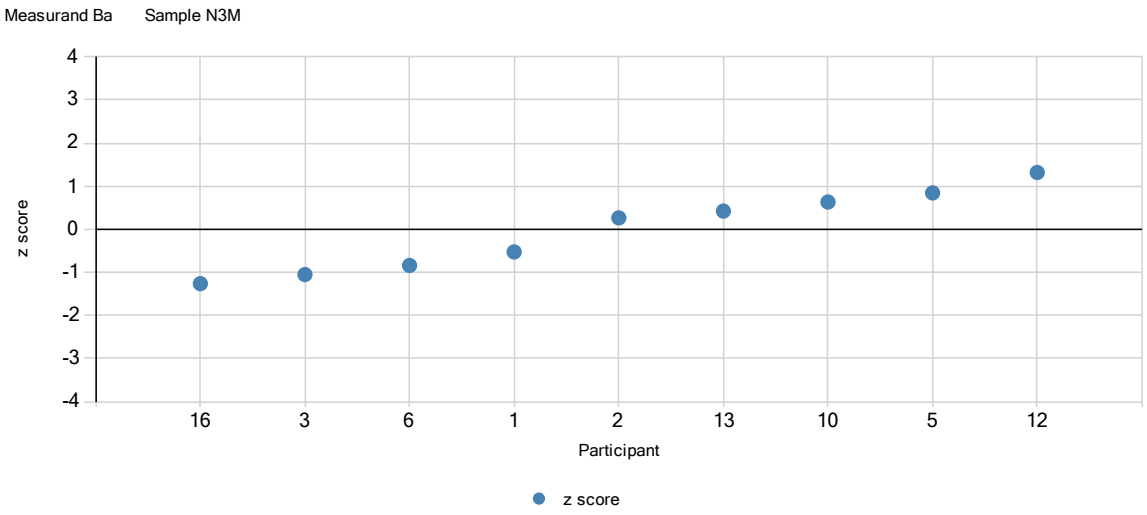


Measurand B Sample N3M

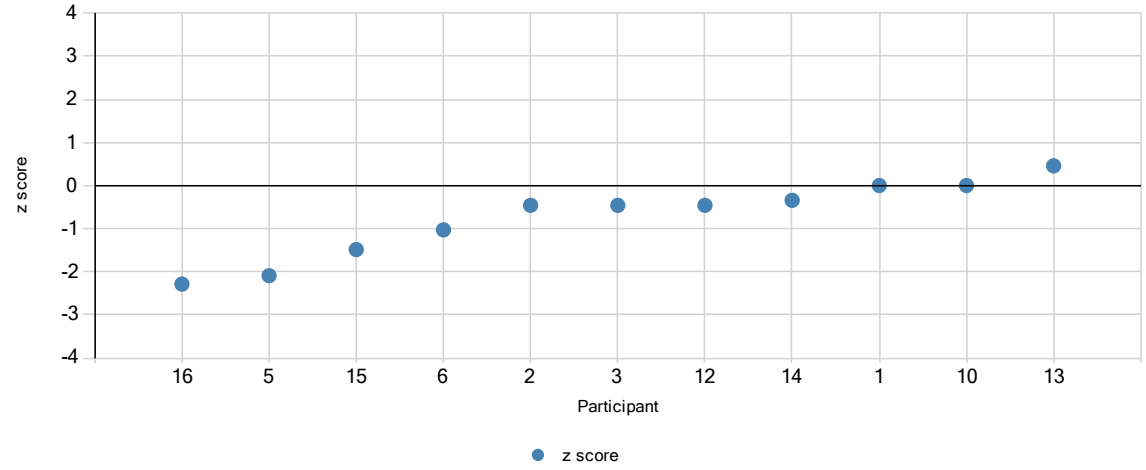



Measurand Ba Sample A1M
z score
4
3
2
1
0
-1
-2
-3
-4
3
6
16
5
2
1
10
13
12
Participant
z score

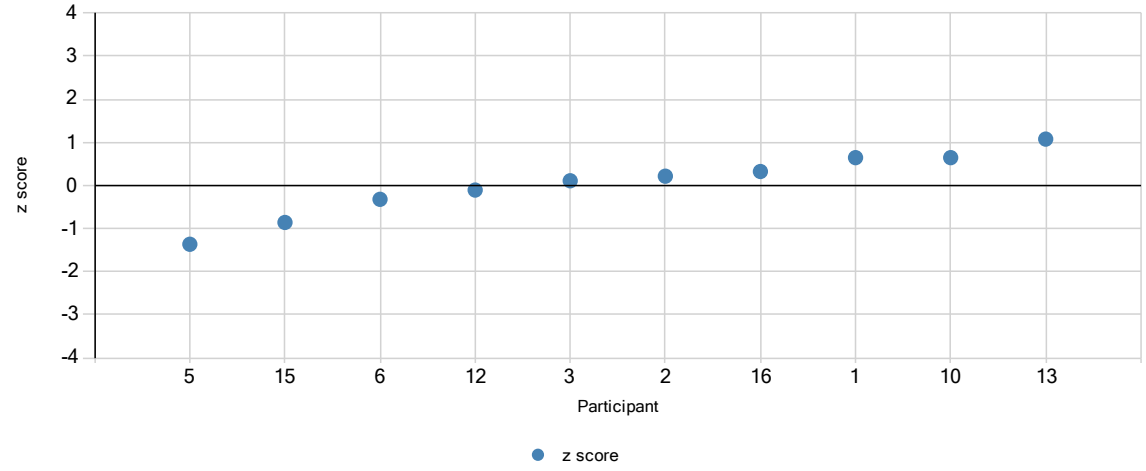

Measurand Ba Sample D2M
z score
4
3
2
1
0
-1
-2
-3
-4
3
16
6
5
2
13
1
10
12
Participant
z score


Measurand Ba Sample N3M
z score
4
3
2
1
0
-1
-2
-3
-4
16
3
6
1
2
13
10
5
12
Participant
z score

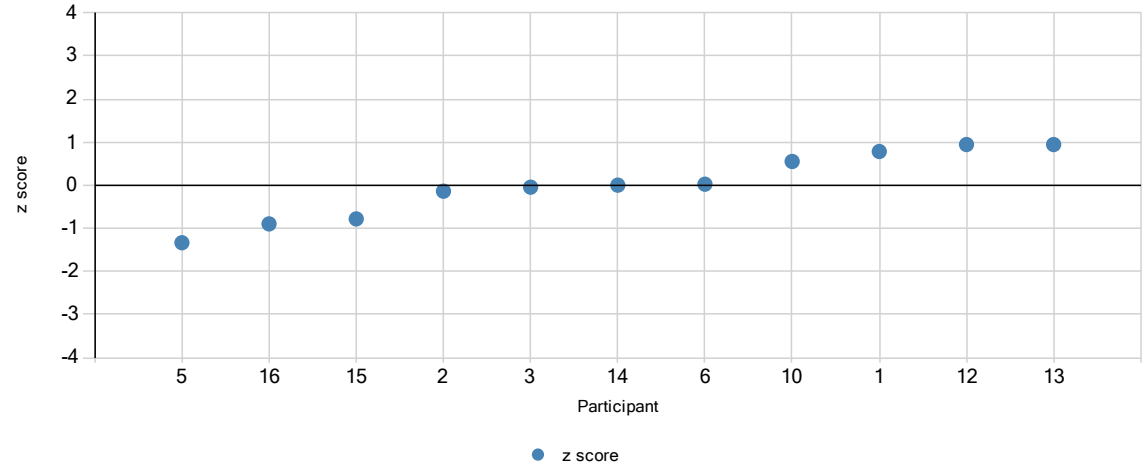
Measurand Ca Sample A1M

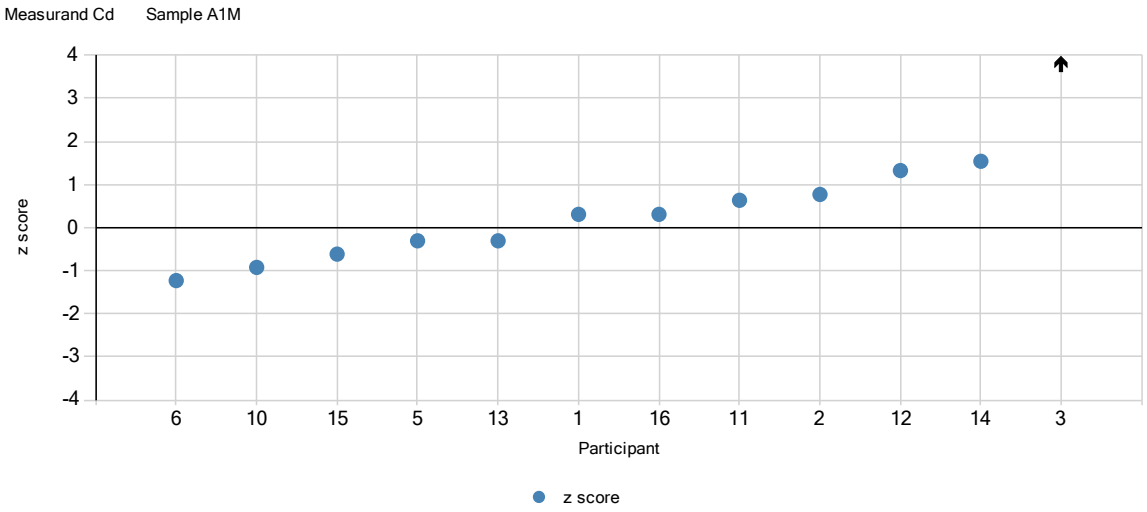


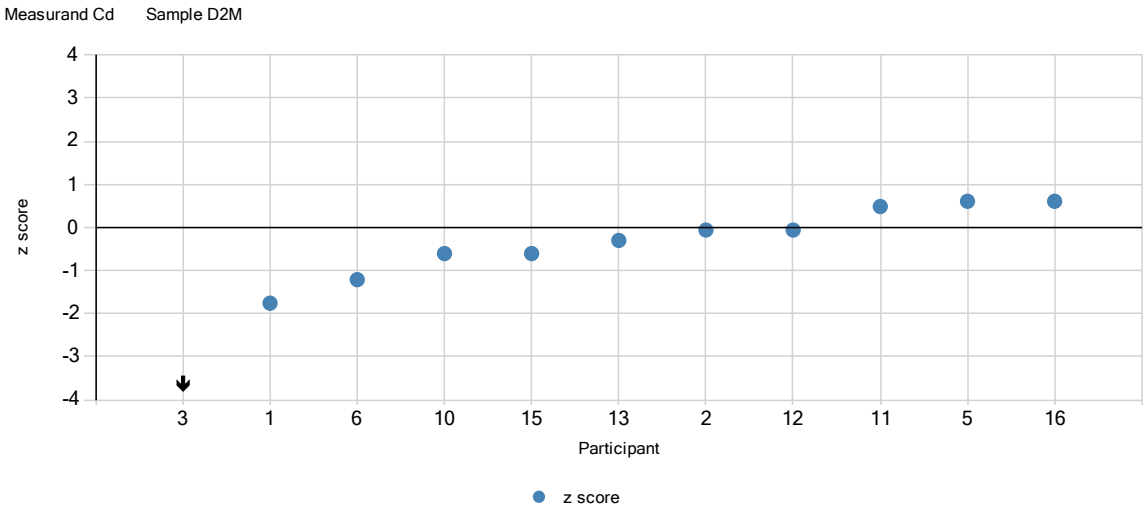
Measurand Ca Sample D2M

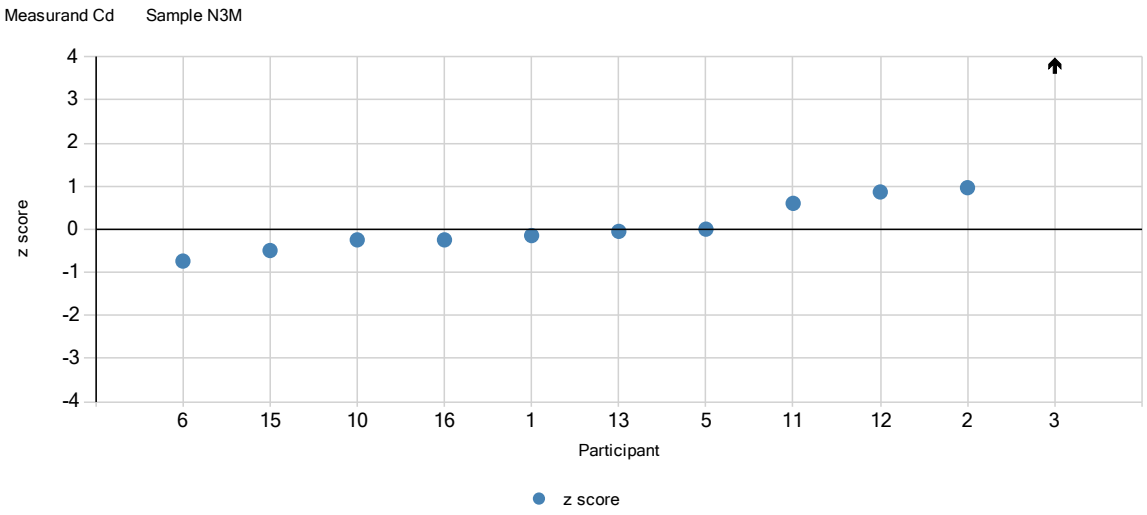


Measurand Ca Sample N3M

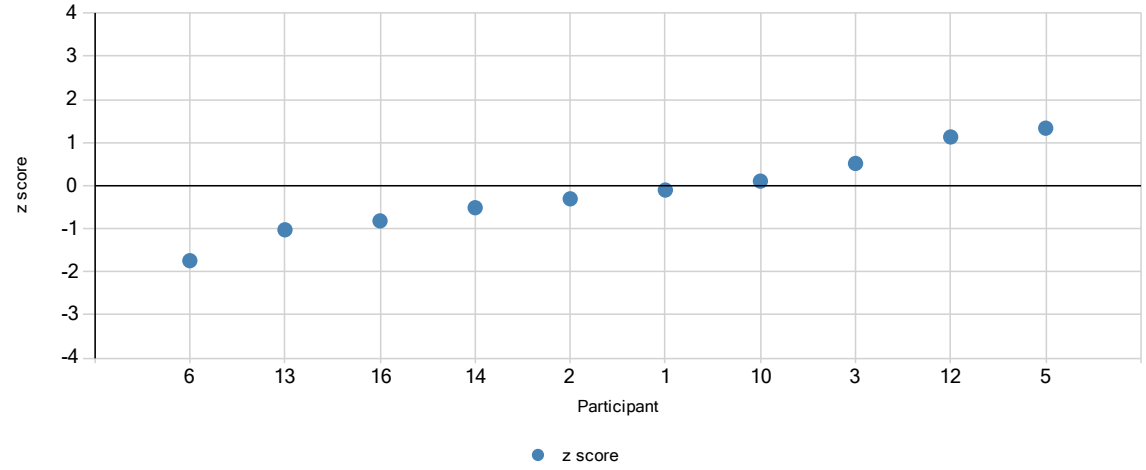



Measurand Cd Sample A1M
4
3
2
1
0
-1
-2
-3
-4
z score
6 10 15 5 13 1 16 11 2 12 14 3
Participant
z score

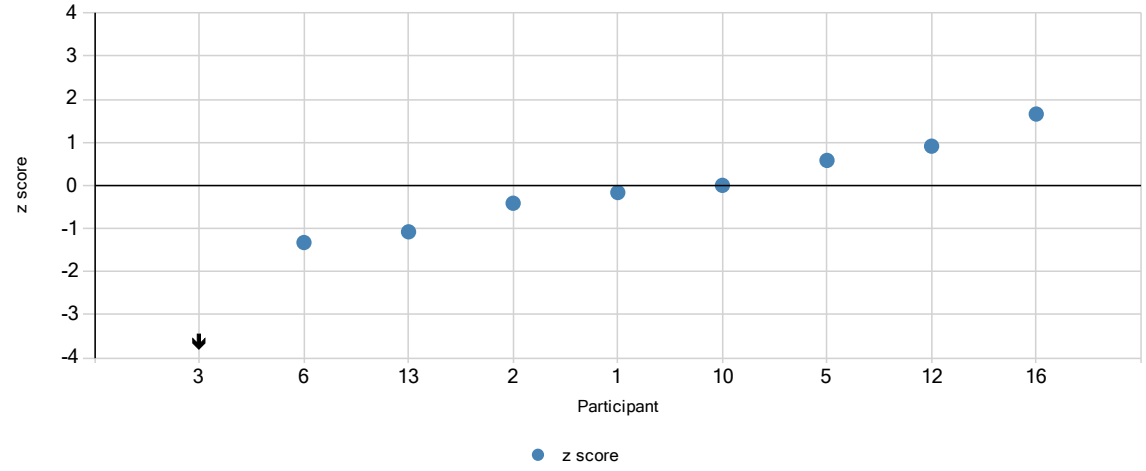

Measurand Cd Sample D2M
4
3
2
1
0
-1
-2
-3
-4
z score
3 1 6 10 15 13 2 12 11 5 16
Participant
z score


Measurand Cd Sample N3M
4
3
2
1
0
-1
-2
-3
-4
z score
6 15 10 16 1 13 5 11 12 2 3
Participant
z score

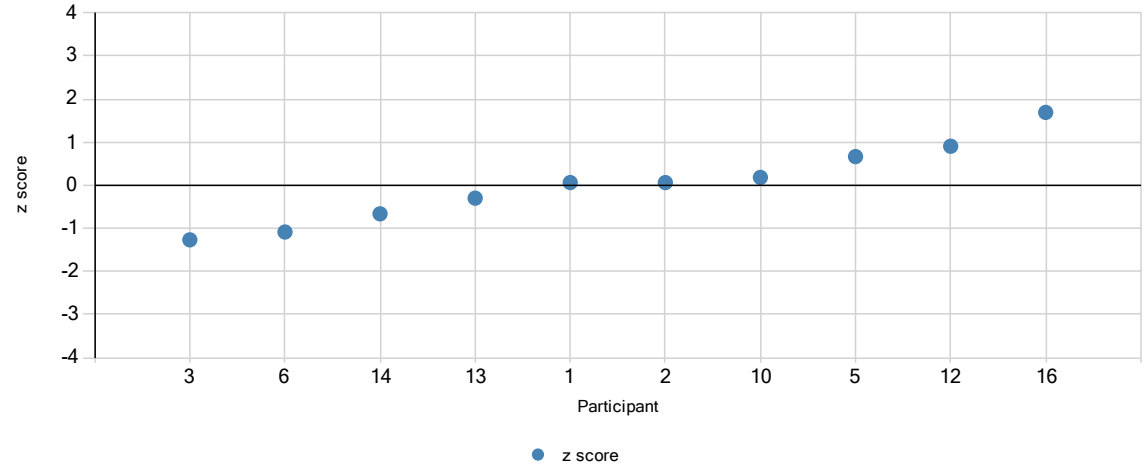
Measurand Co Sample A1M

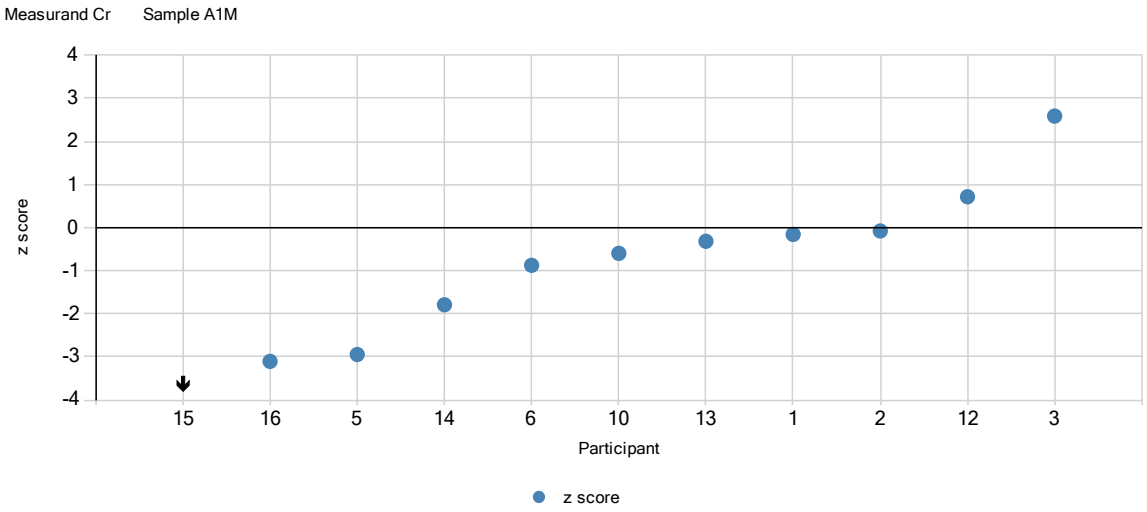


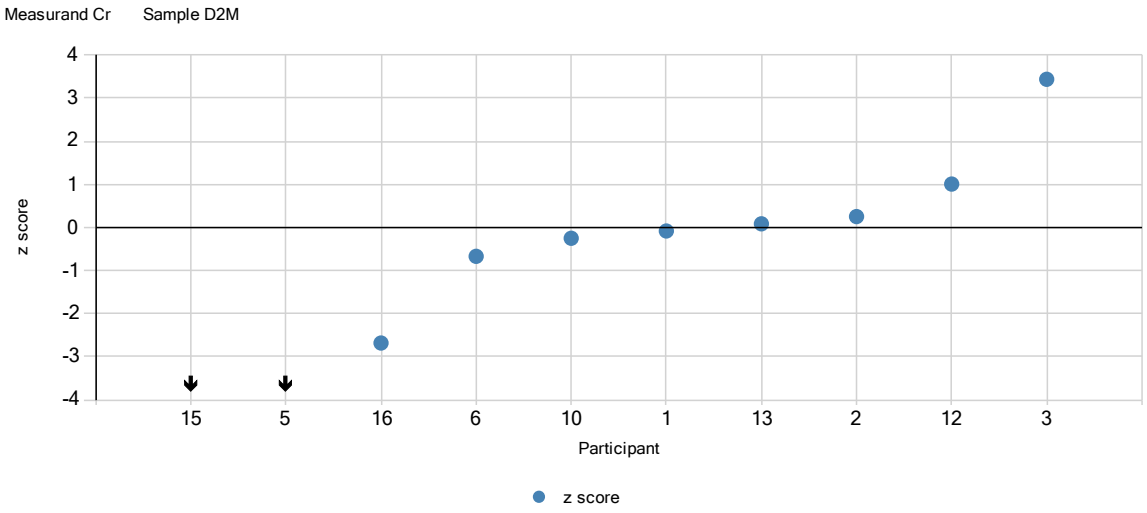
Measurand Co Sample D2M

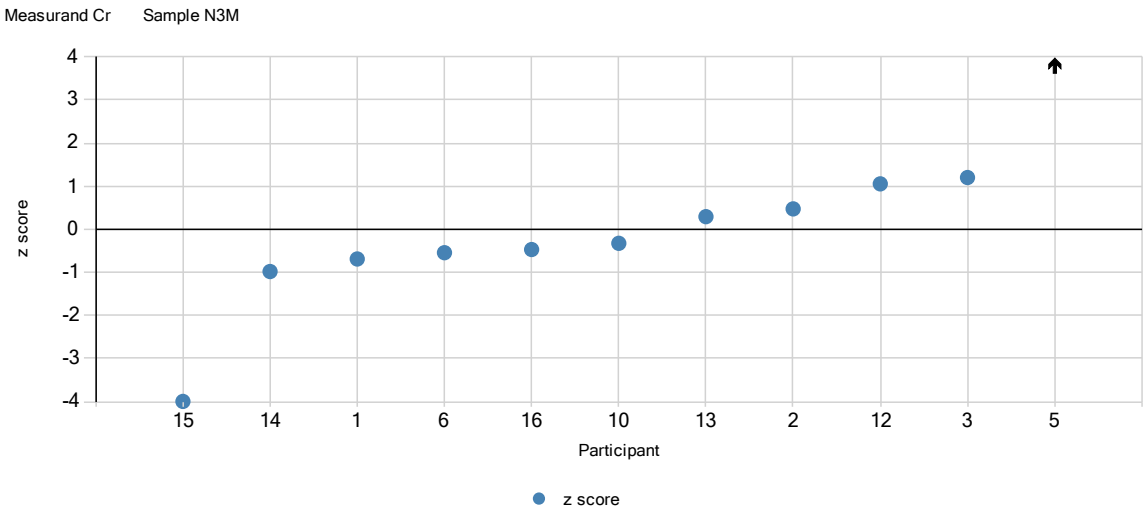


Measurand Co Sample N3M

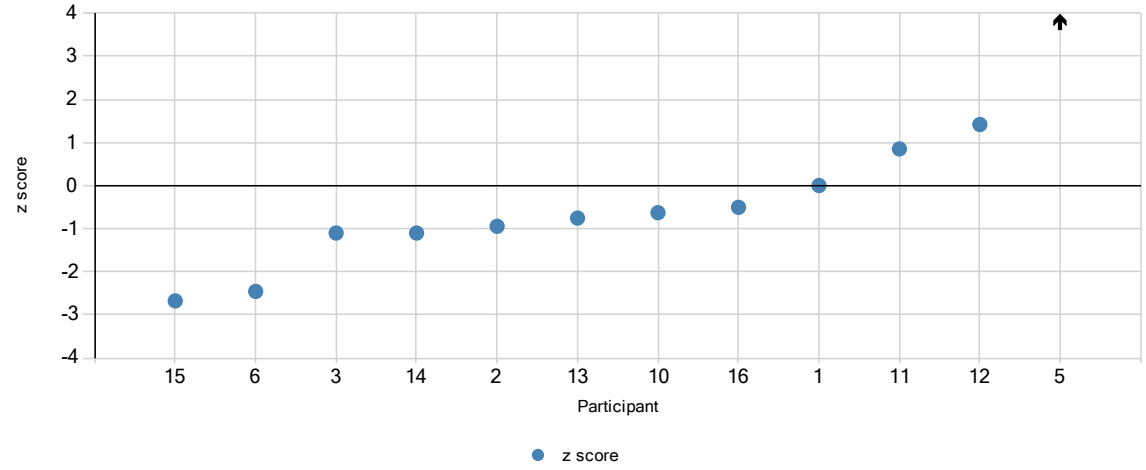



Measurand Cr Sample A1M
z score
4
3
2
1
0
-1
-2
-3
-4
15 16 5 14 6 10 13 1 2 12 3
Participant
z score

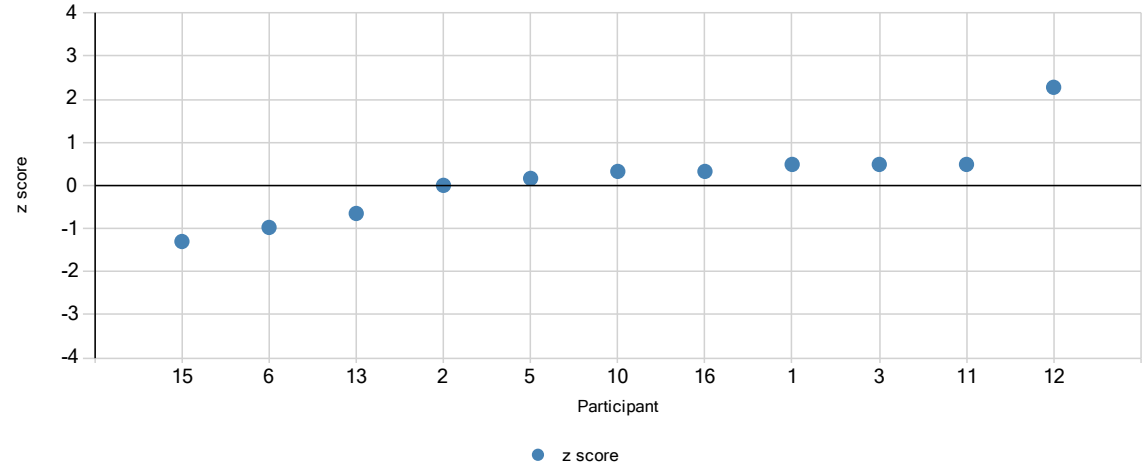

Measurand Cr Sample D2M
z score
4
3
2
1
0
-1
-2
-3
-4
15 5 16 6 10 1 13 2 12 3
Participant
z score


Measurand Cr Sample N3M
z score
4
3
2
1
0
-1
-2
-3
-4
15 14 1 6 16 10 13 2 12 3 5
Participant
z score

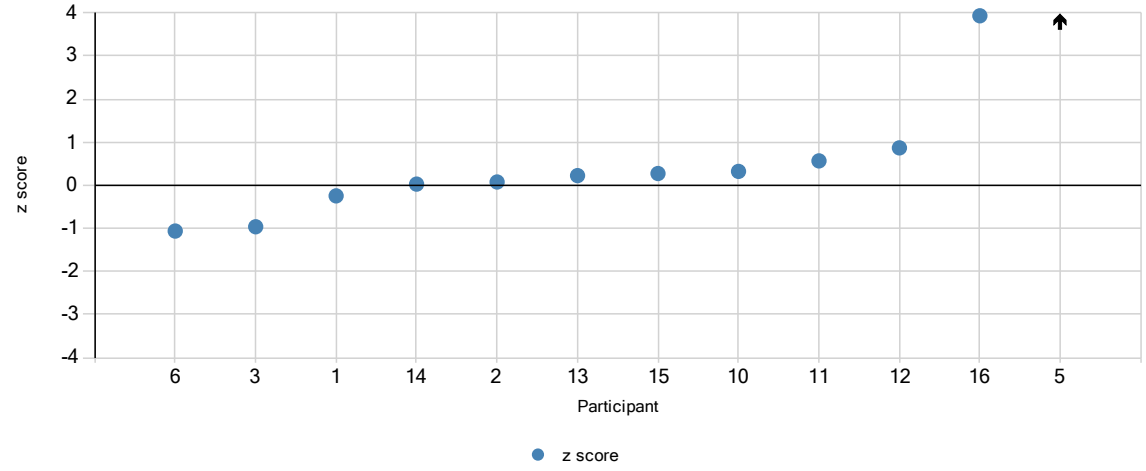
Measurand Cu Sample A1M

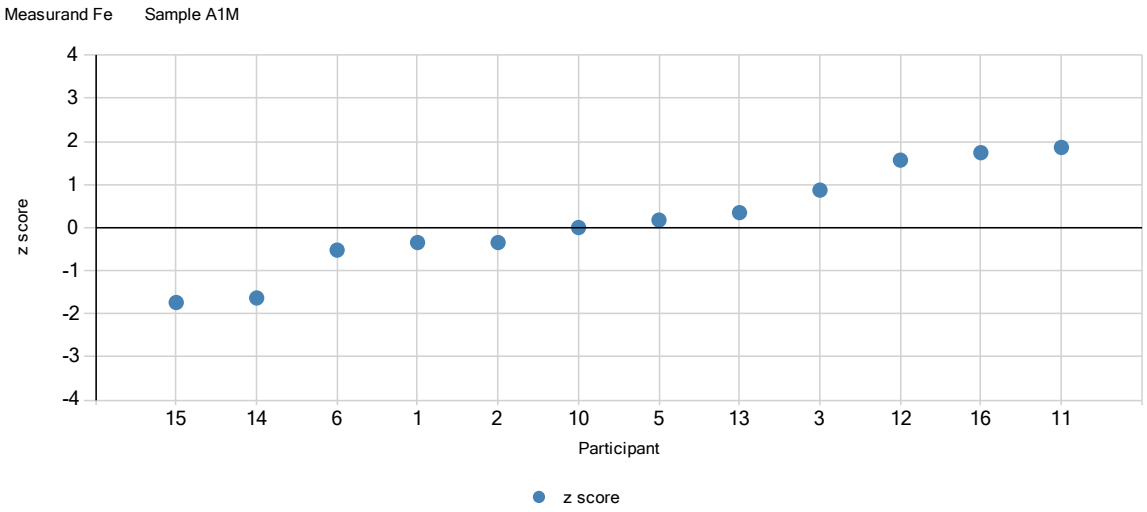


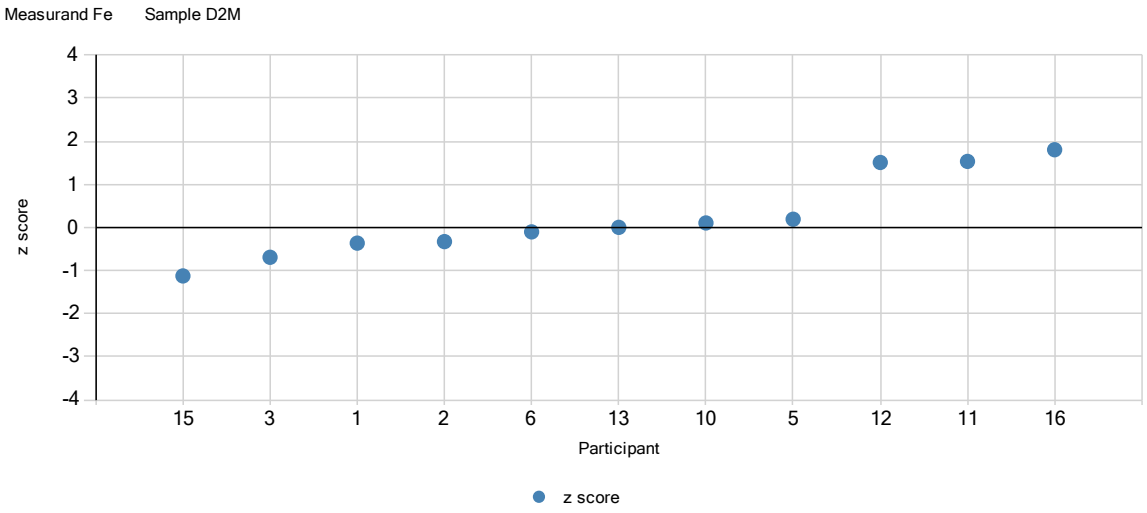
Measurand Cu Sample D2M

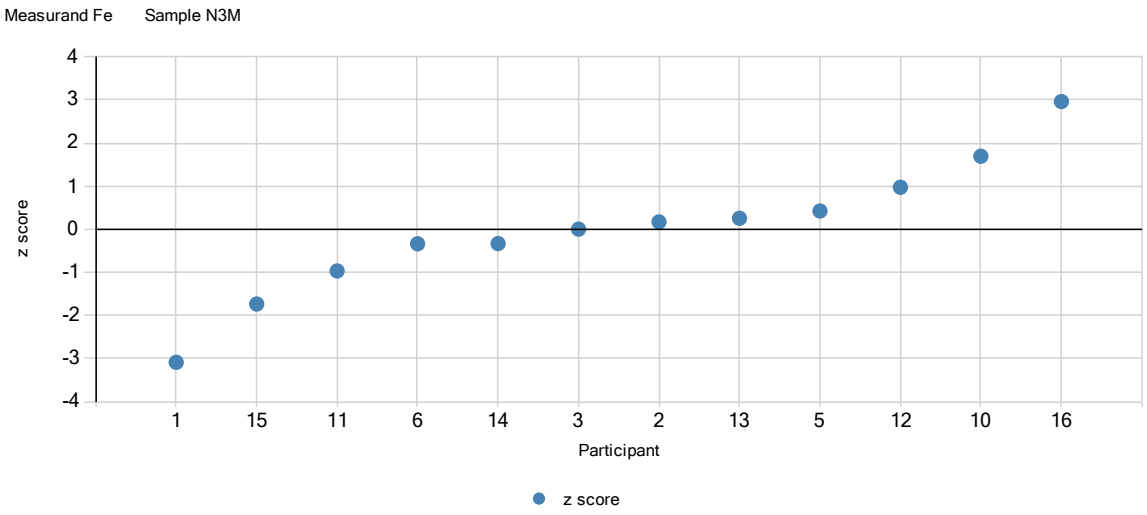


Measurand Cu Sample N3M

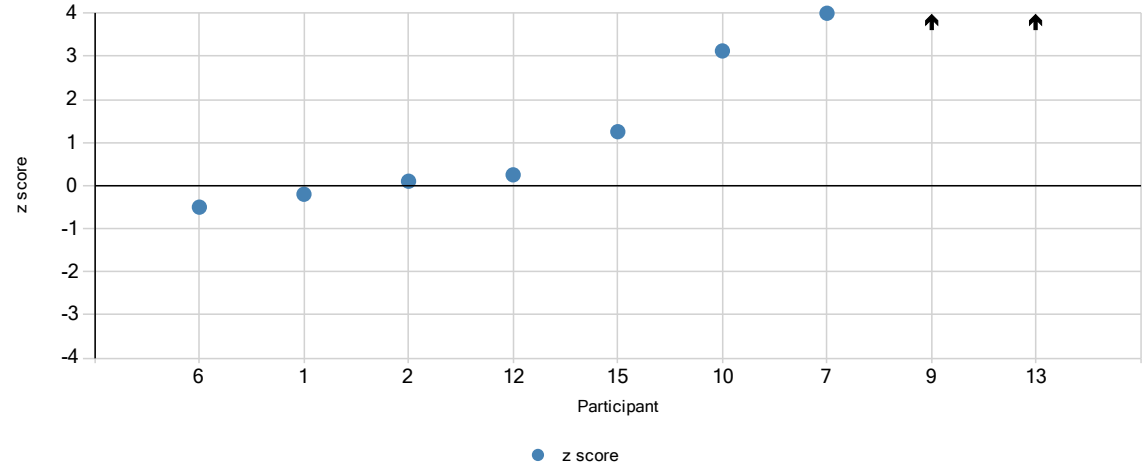



Measurand Fe Sample A1M
z score
4
3
2
1
0
-1
-2
-3
-4
15 14 6 1 2 10 5 13 3 12 16 11
Participant
z score

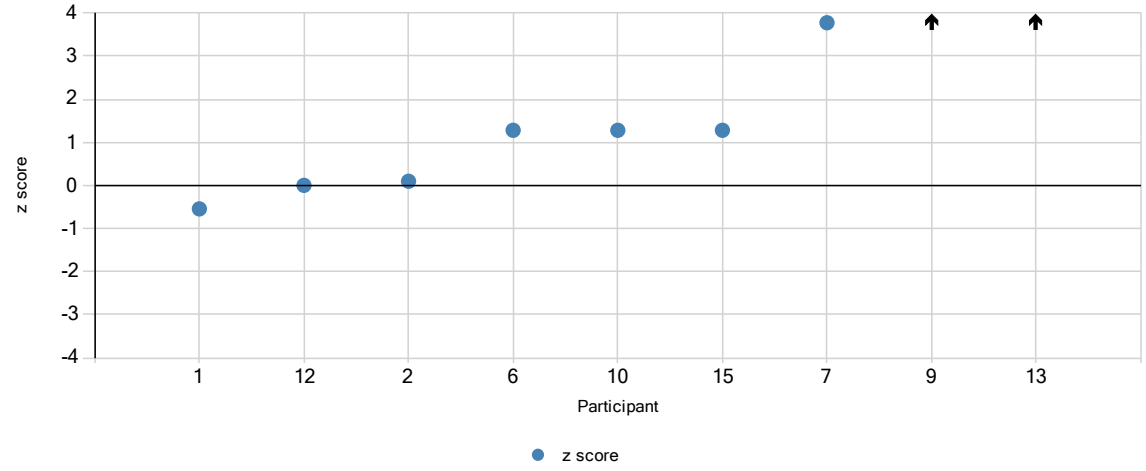

Measurand Fe Sample D2M
z score
4
3
2
1
0
-1
-2
-3
-4
15 3 1 2 6 13 10 5 12 11 16
Participant
z score


Measurand Fe Sample N3M
z score
4
3
2
1
0
-1
-2
-3
-4
1 15 11 6 14 3 2 13 5 12 10 16
Participant
z score

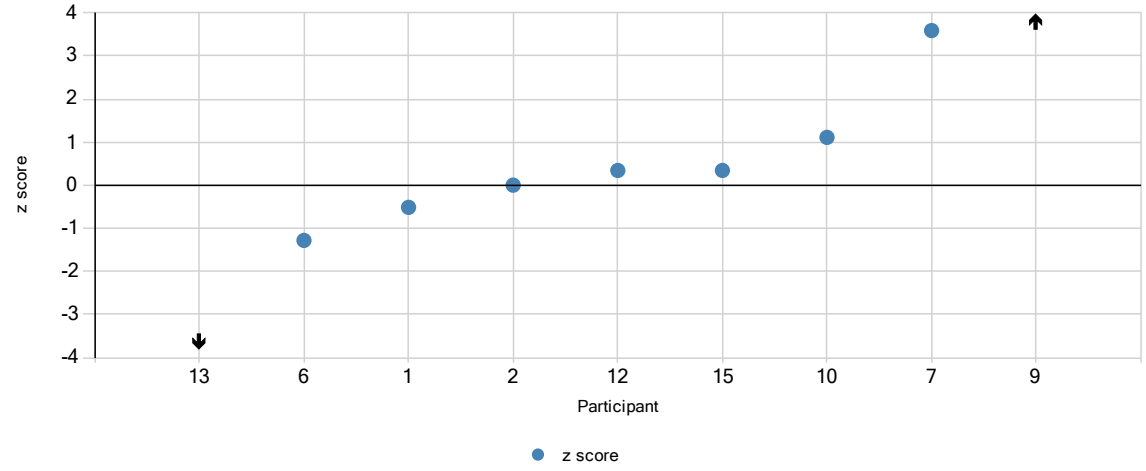
Measurand Hg Sample A1Hg



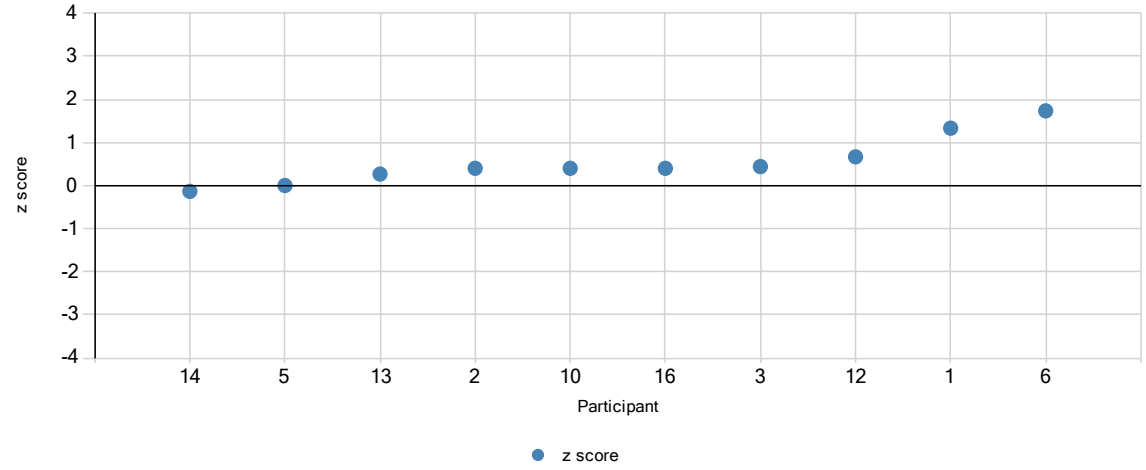
Measurand Hg Sample D2Hg



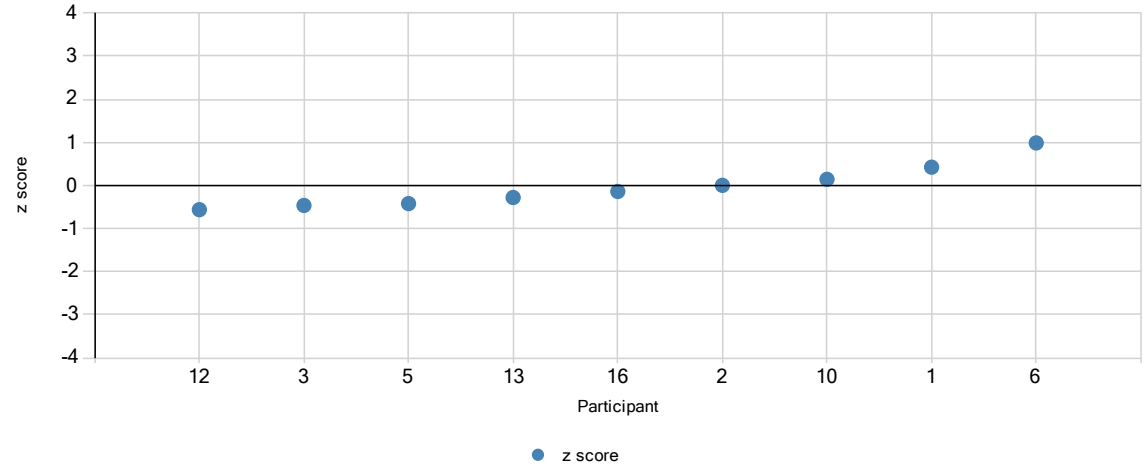
Measurand Hg Sample N3Hg



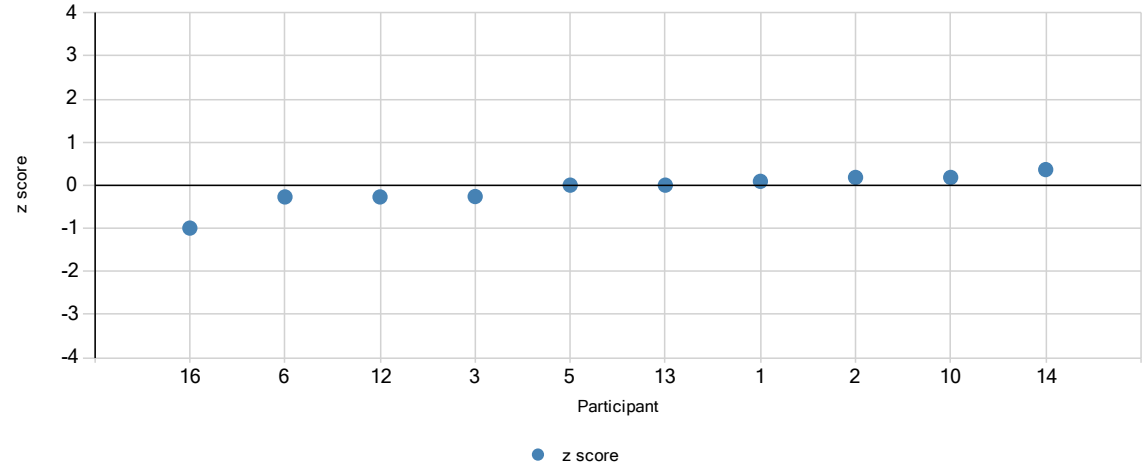
Measurand K Sample A1M



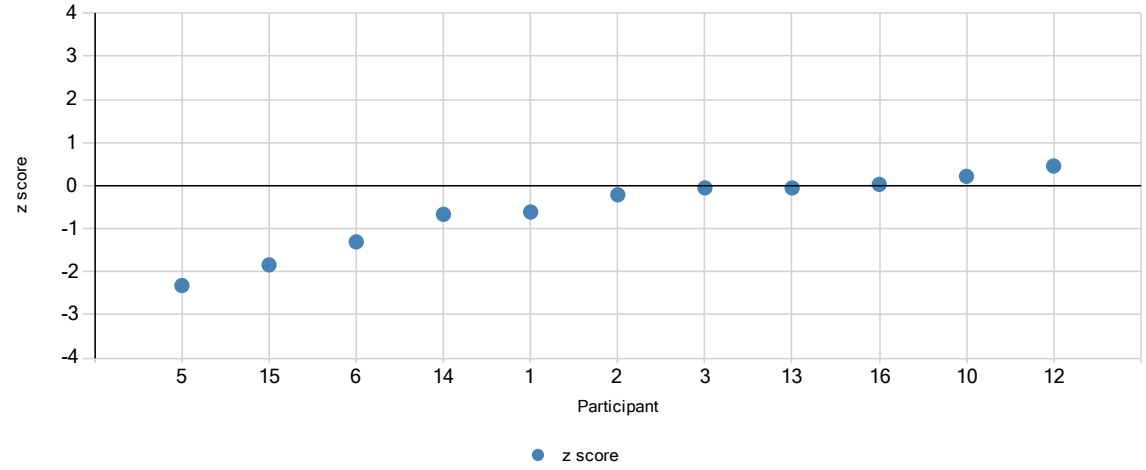
Measurand K Sample D2M



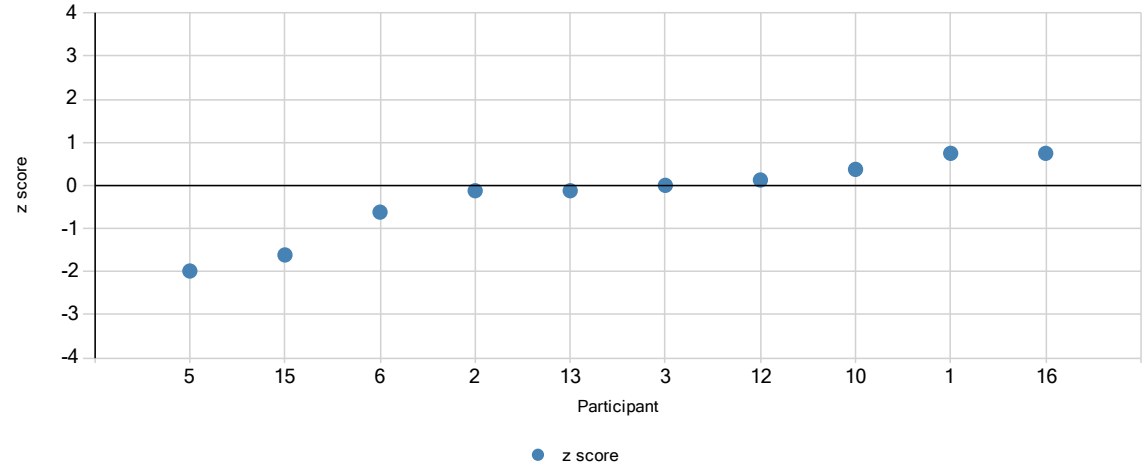
Measurand K Sample N3M



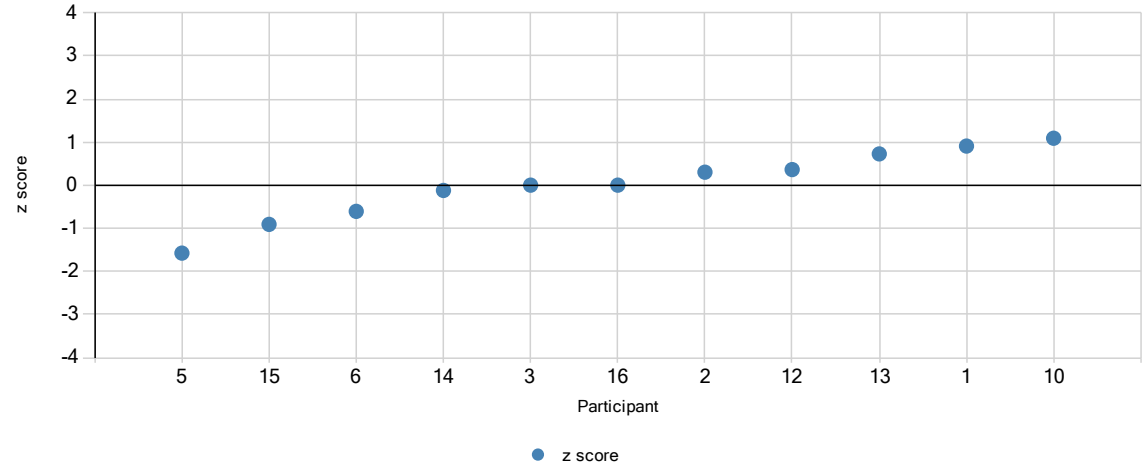
Measurand Mg Sample A1M



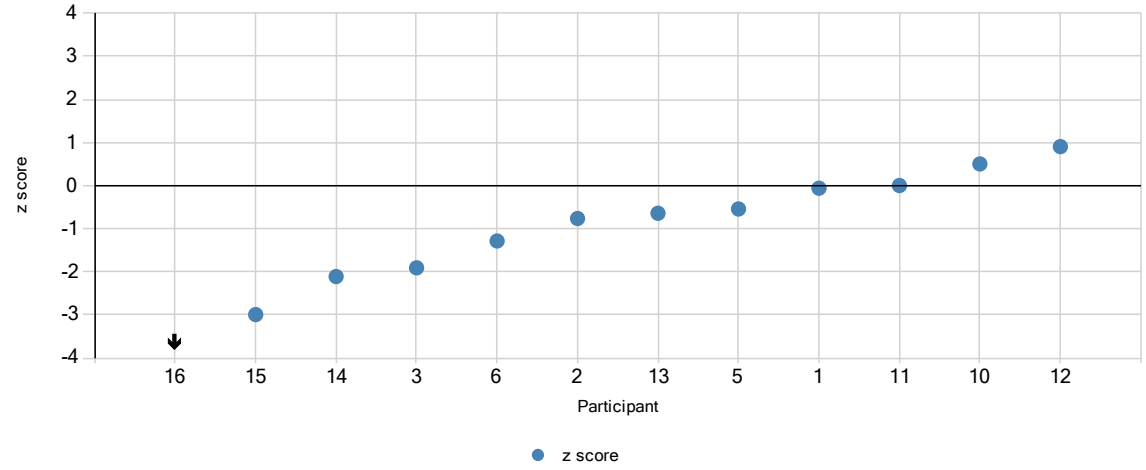
Measurand Mg Sample D2M



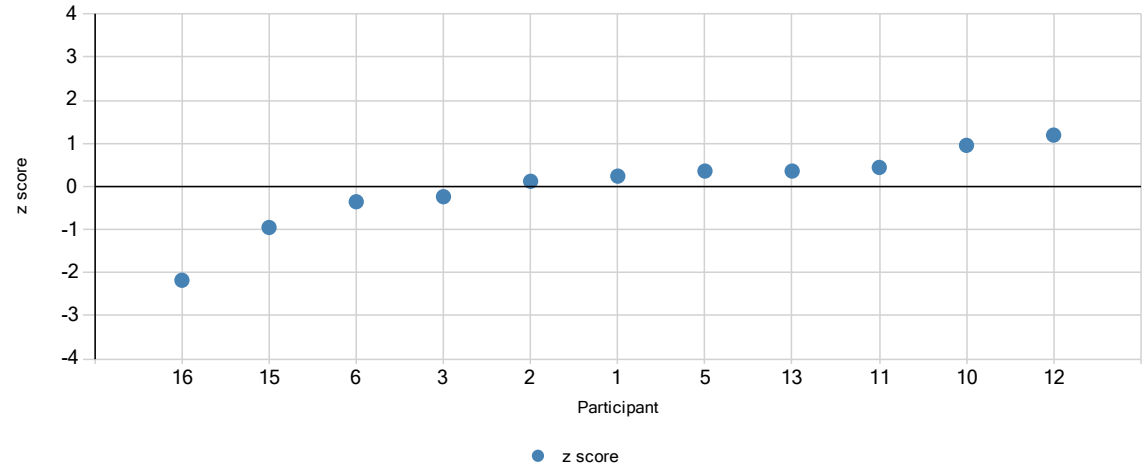
Measurand Mg Sample N3M



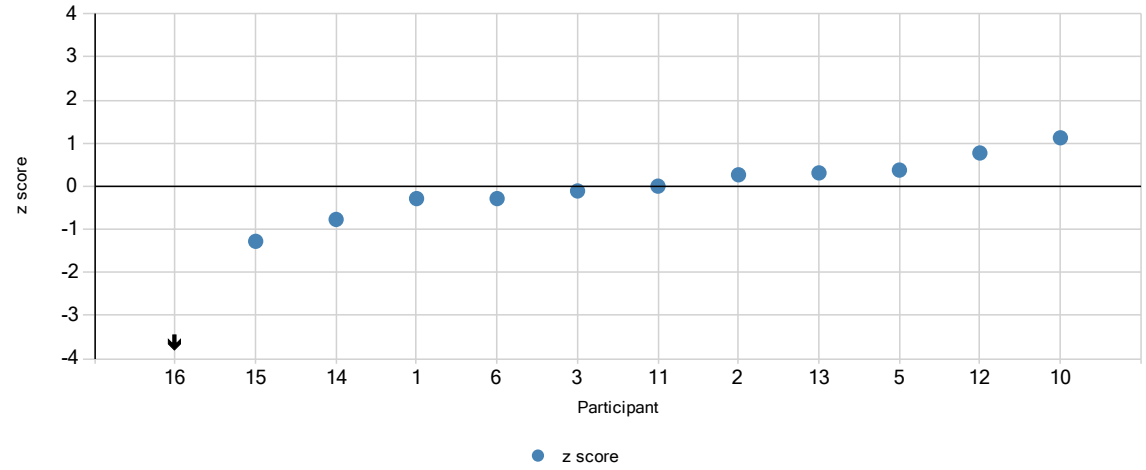
Measurand Mn Sample A1M



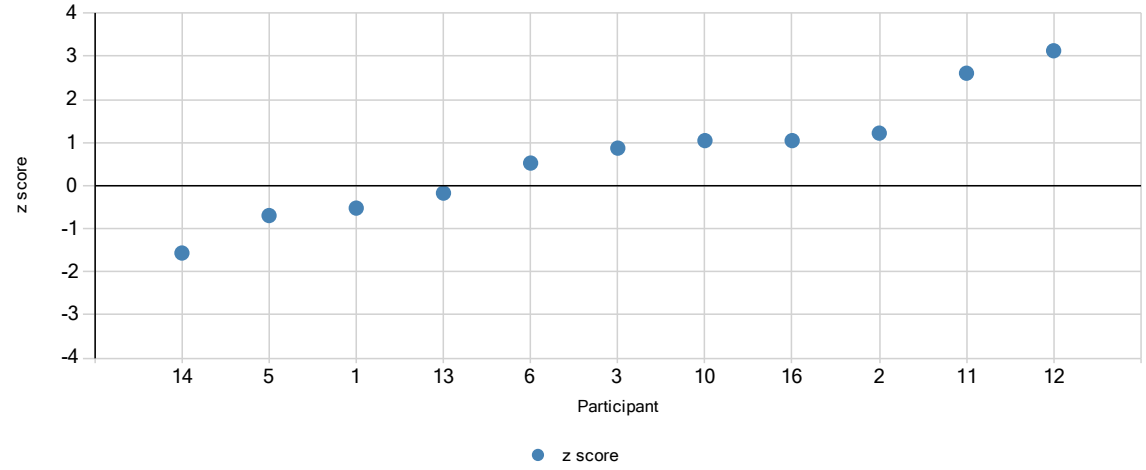
Measurand Mn Sample D2M



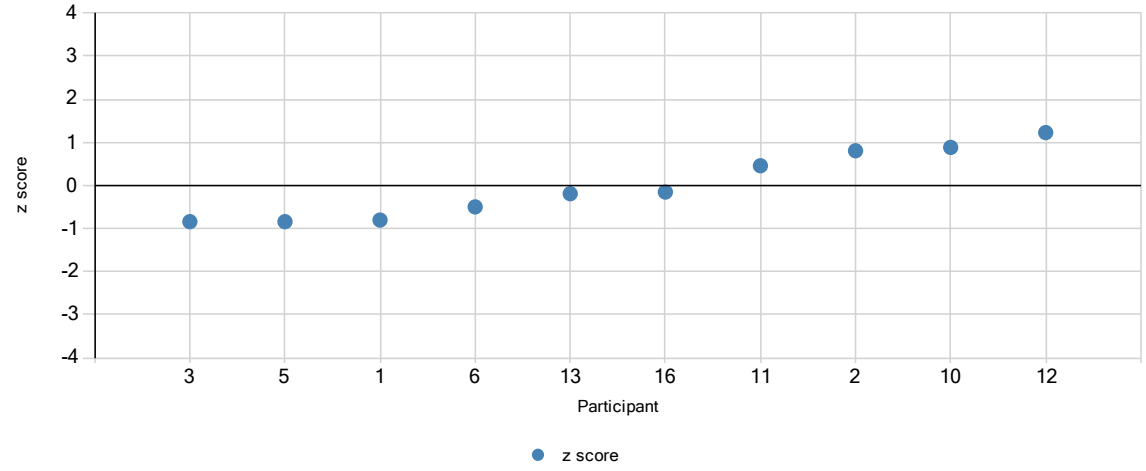
Measurand Mn Sample N3M



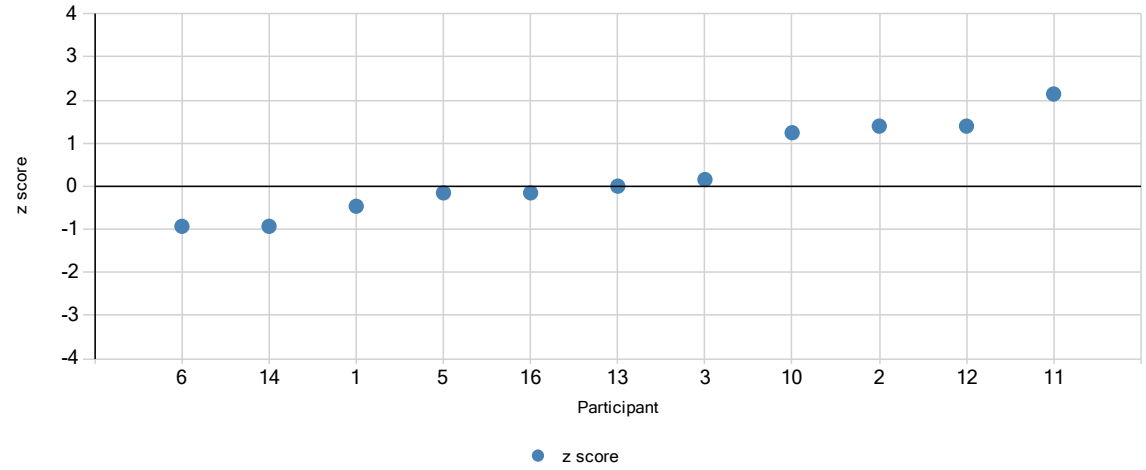
Measurand Mo Sample A1M



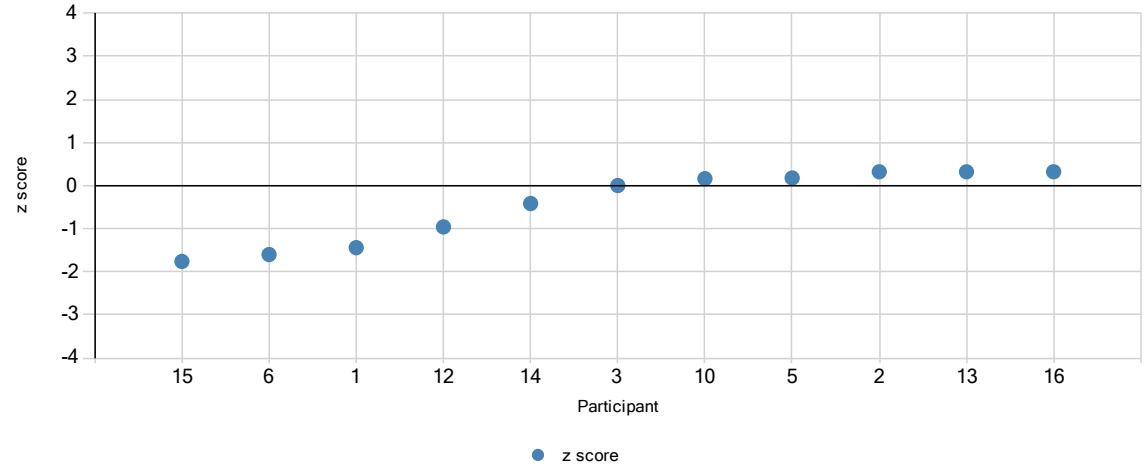
Measurand Mo Sample D2M



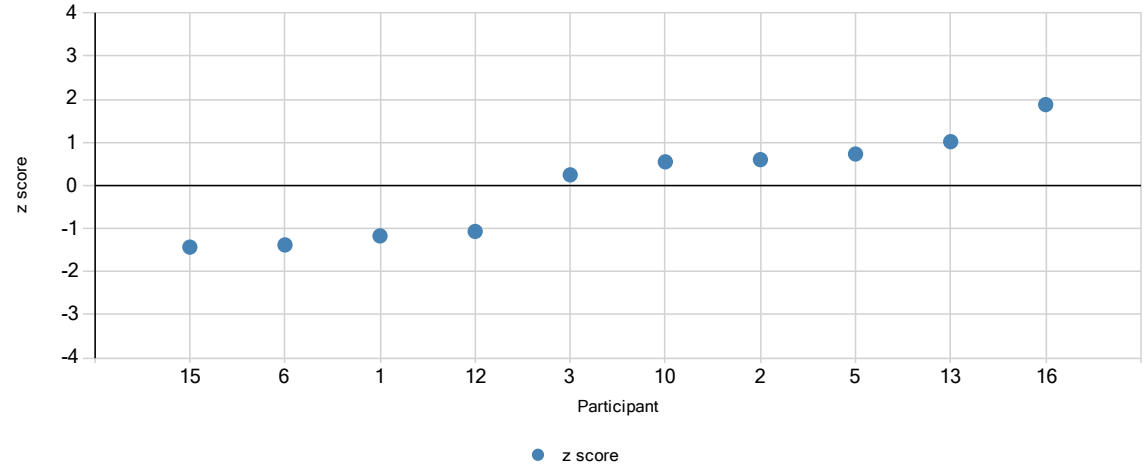
Measurand Mo Sample N3M



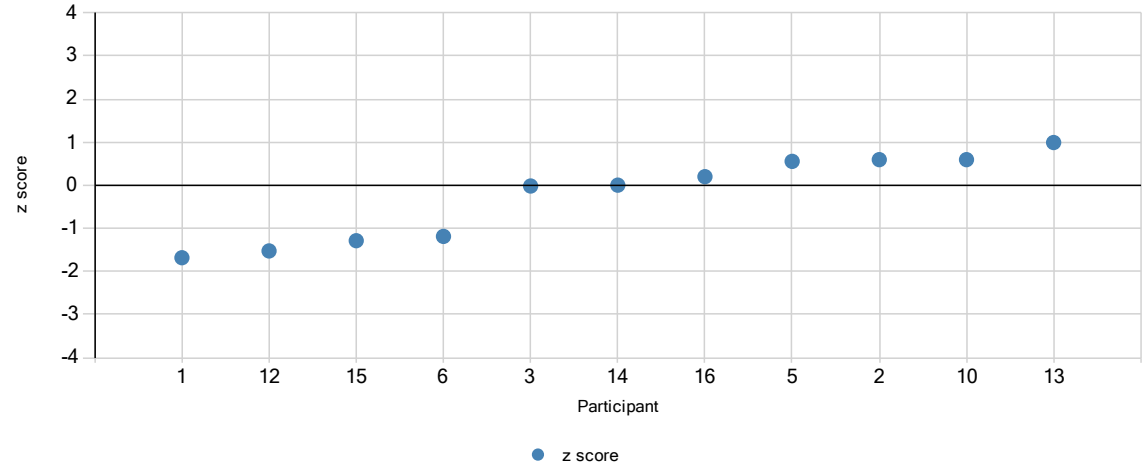
Measurand Na Sample A1M



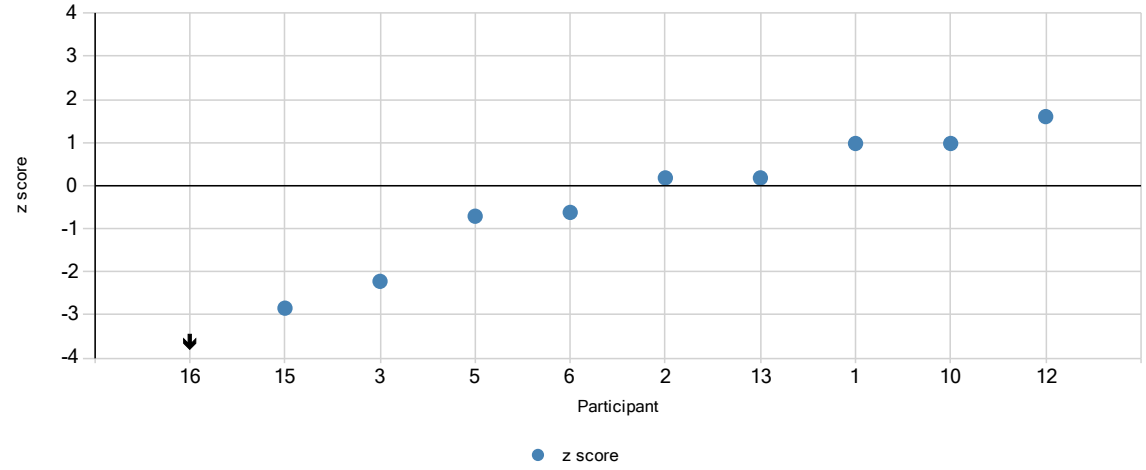
Measurand Na Sample D2M



Measurand Na Sample N3M



Measurand Ni Sample A1M



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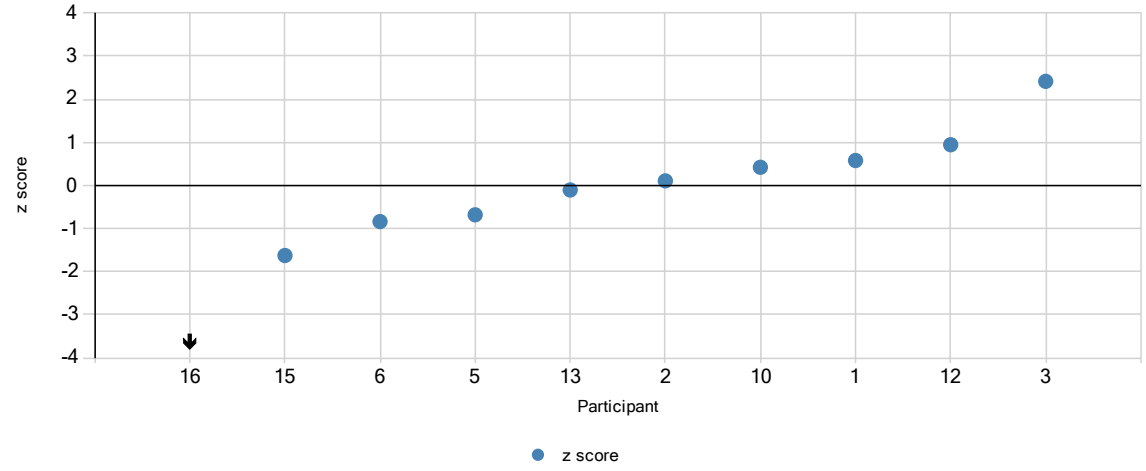
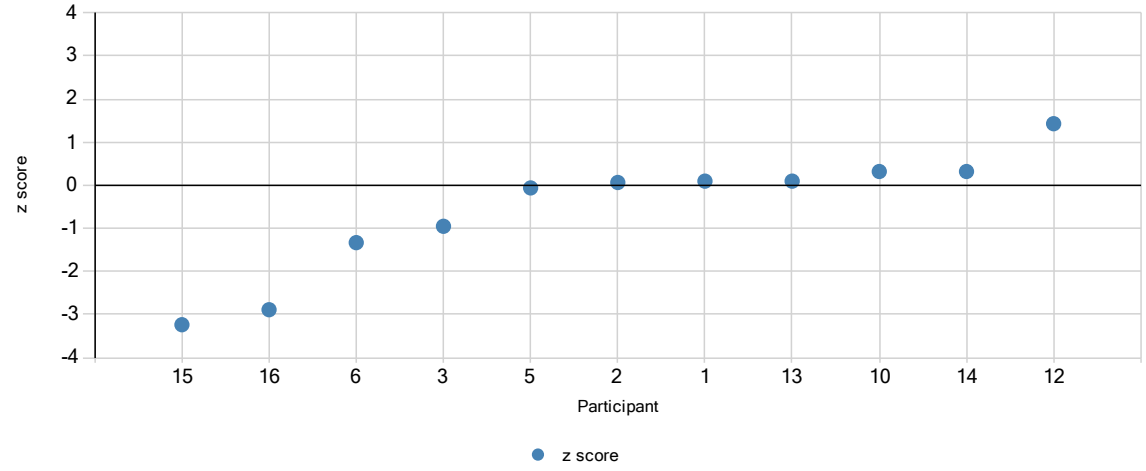
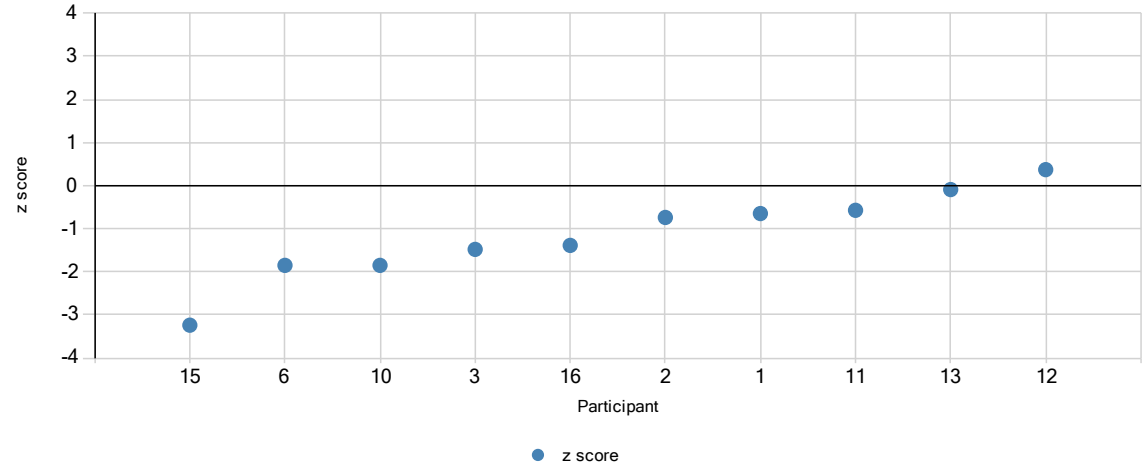


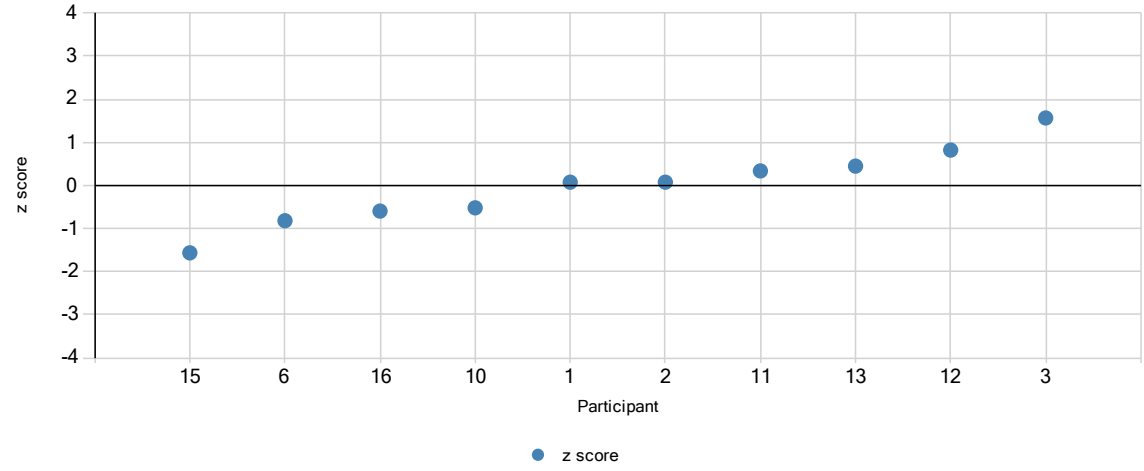
Measurand Ni Sample N3M



Measurand Pb Sample A1M



Measurand Pb Sample D2M



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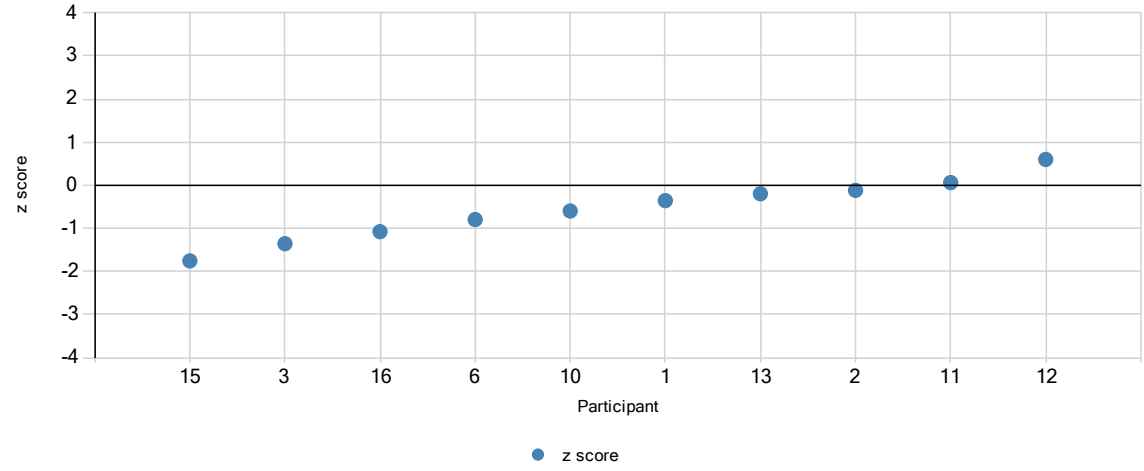
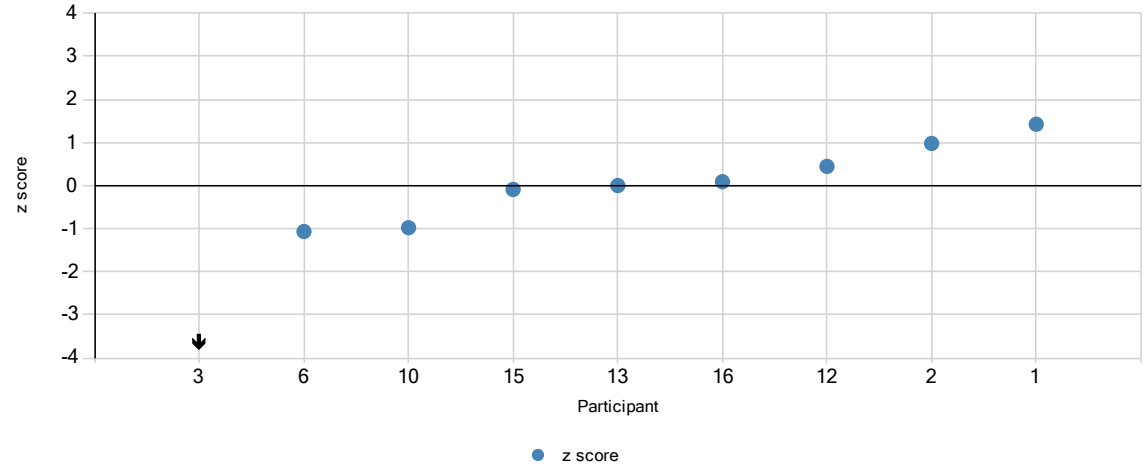
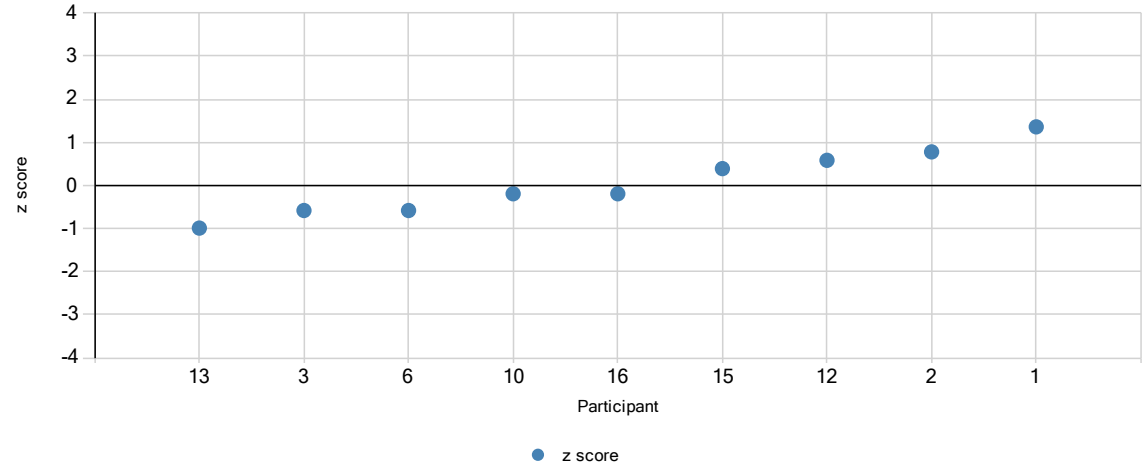


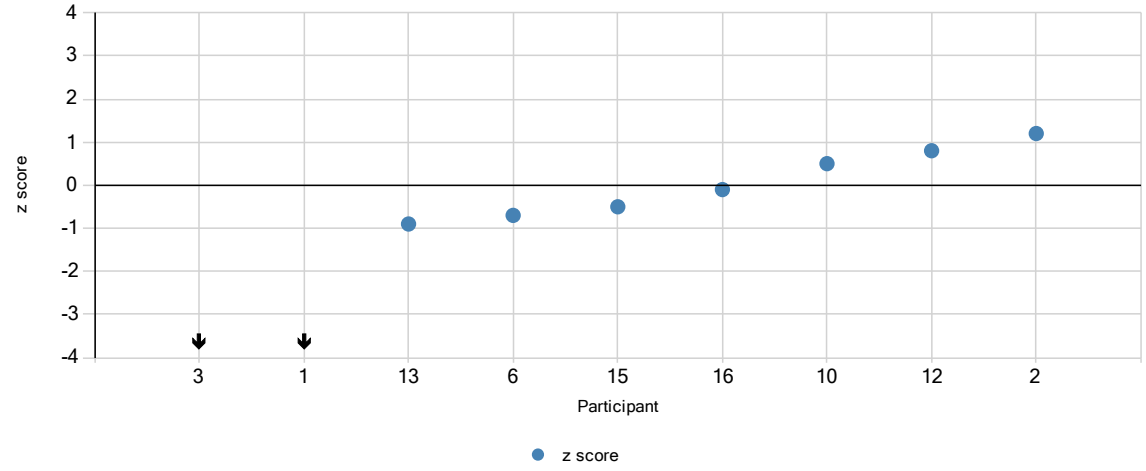
Measurand Sb Sample A1M



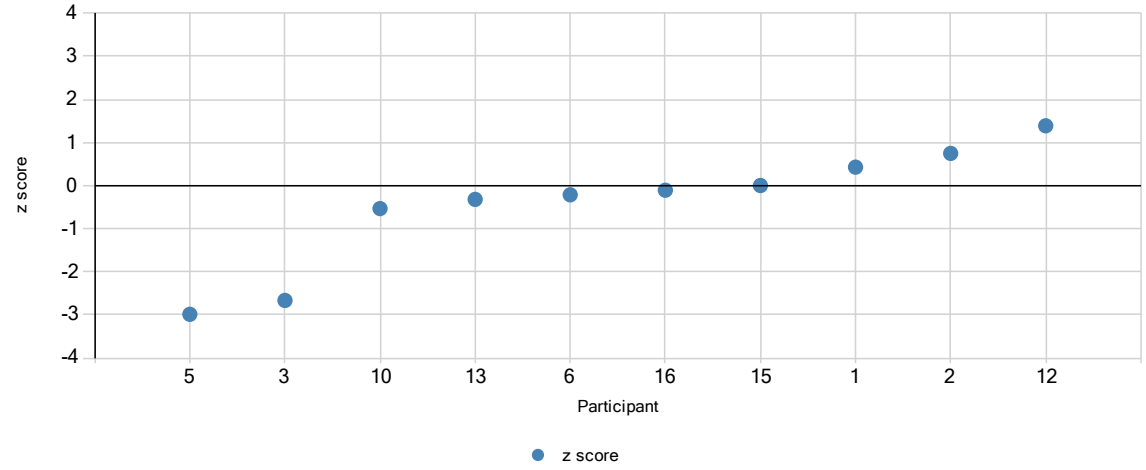
Measurand Sb Sample D2M



Measurand Sb Sample N3M



Measurand Se Sample A1M



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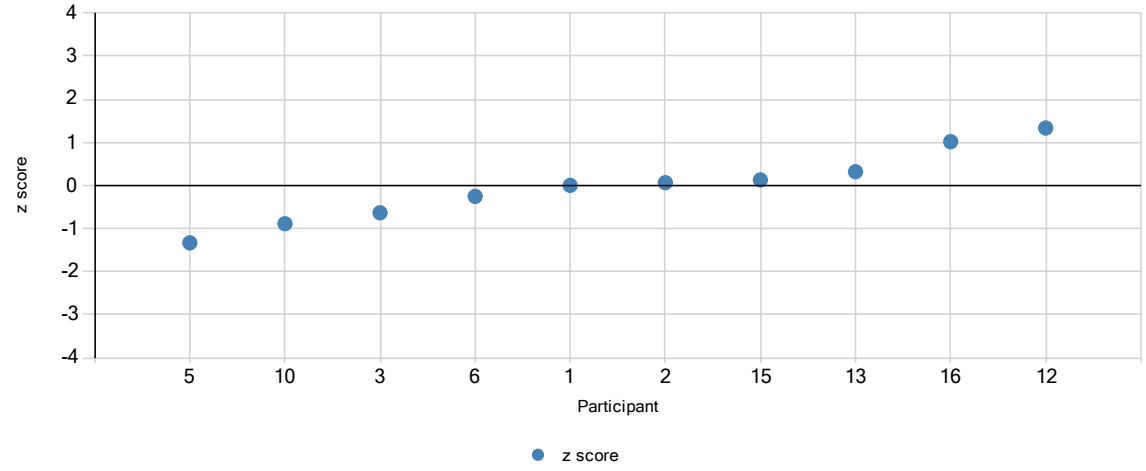

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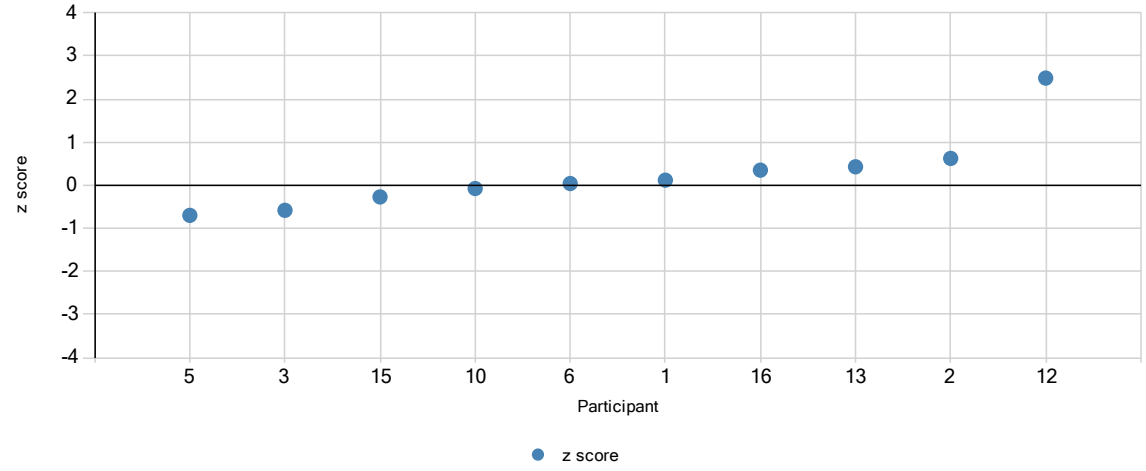
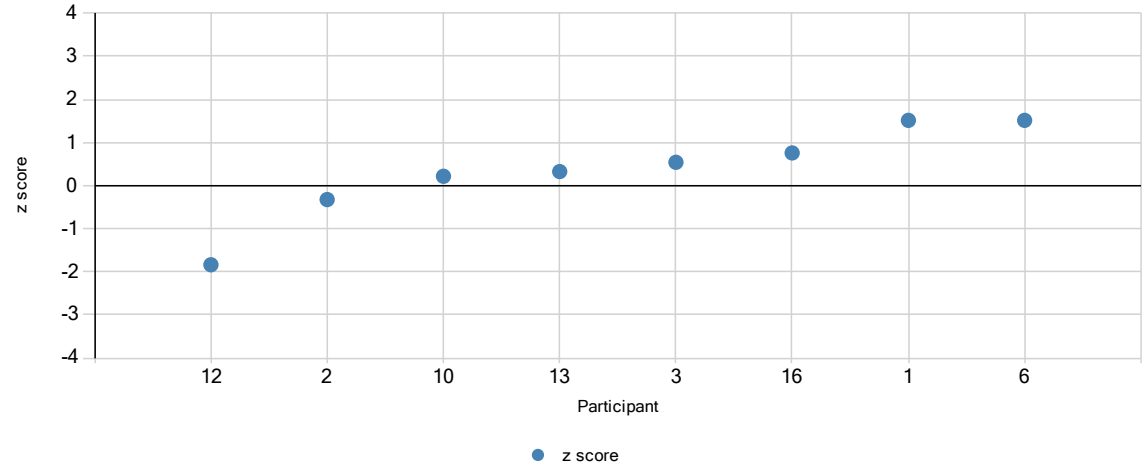


Measurand Ti Sample A1M



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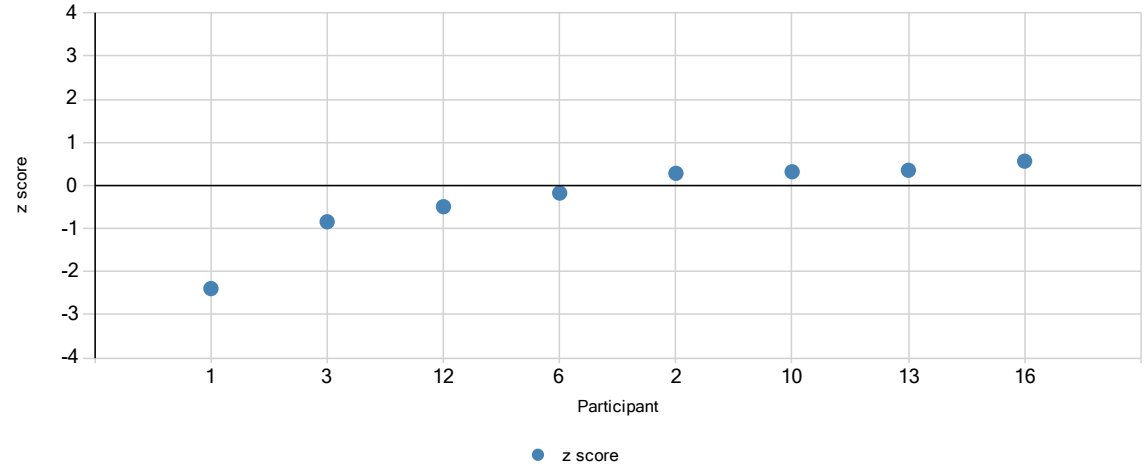
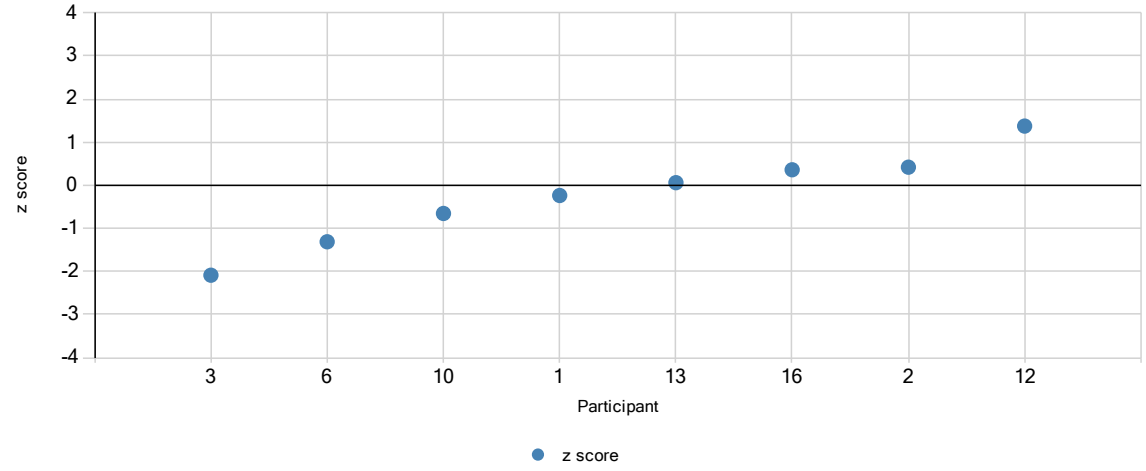


Measurand V Sample A1M



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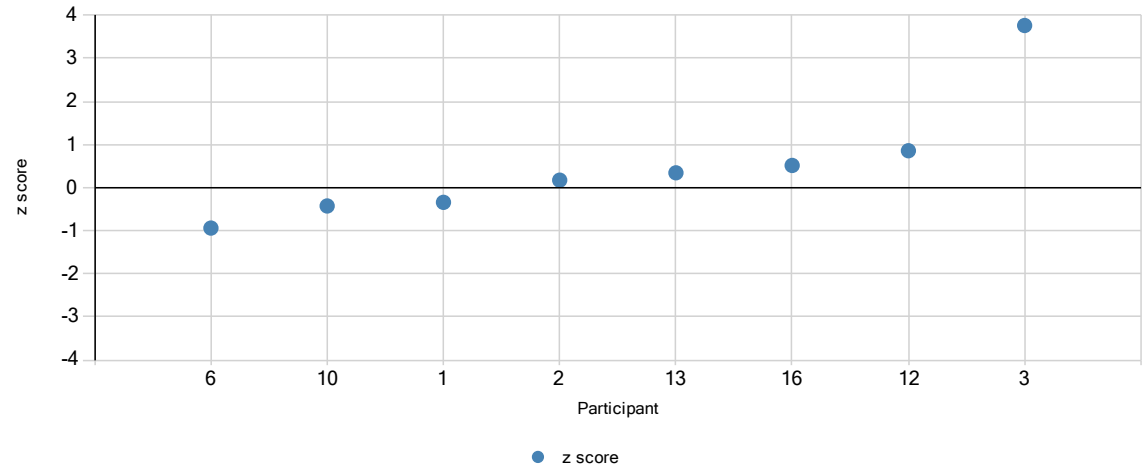
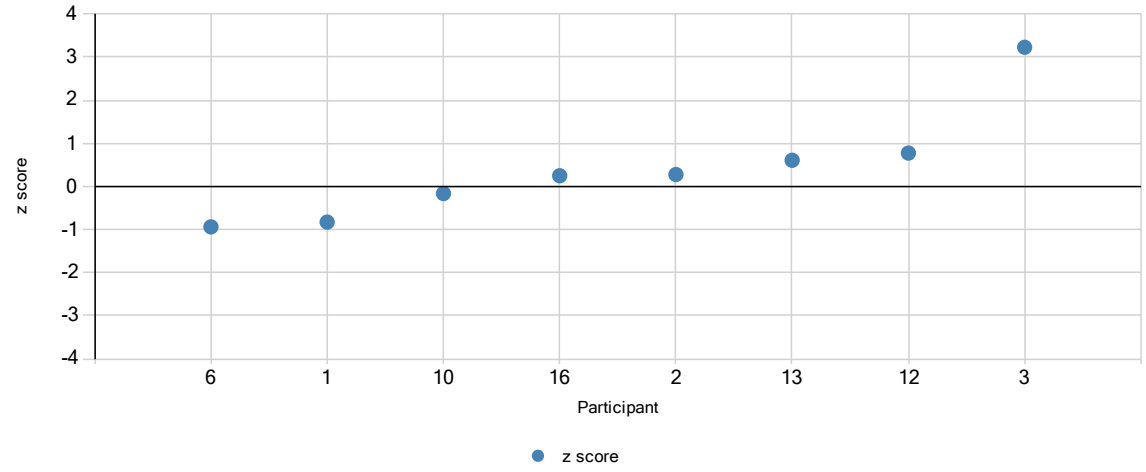
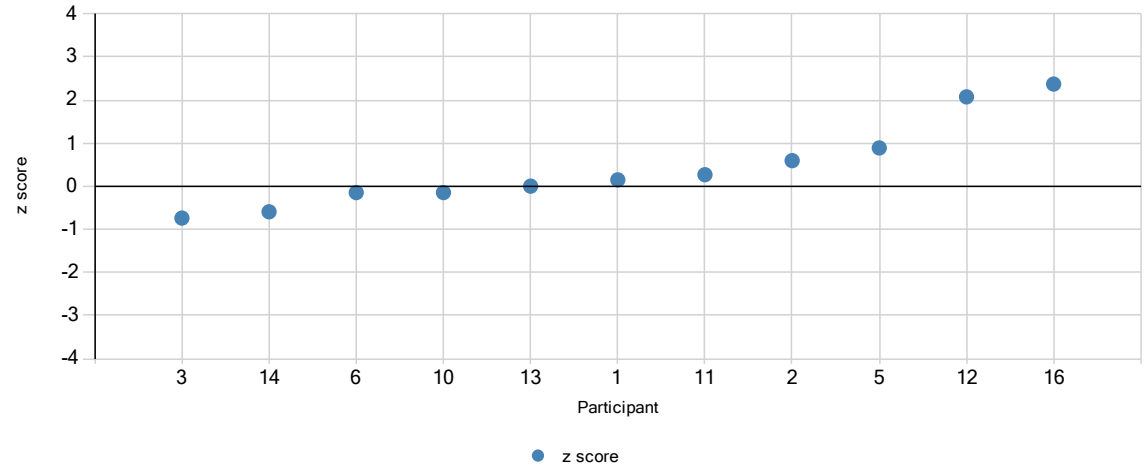


Measurand V Sample N3M



Measurand Zn Sample A1M



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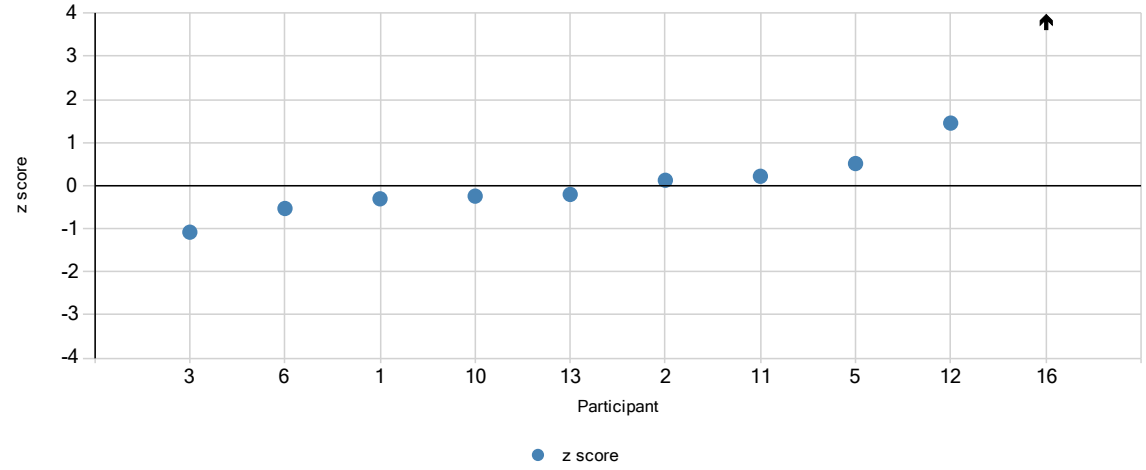

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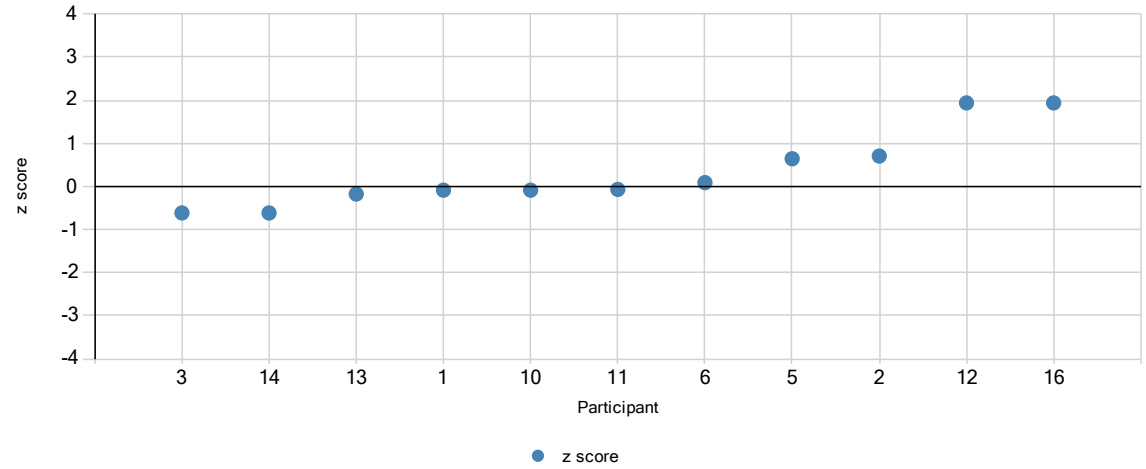
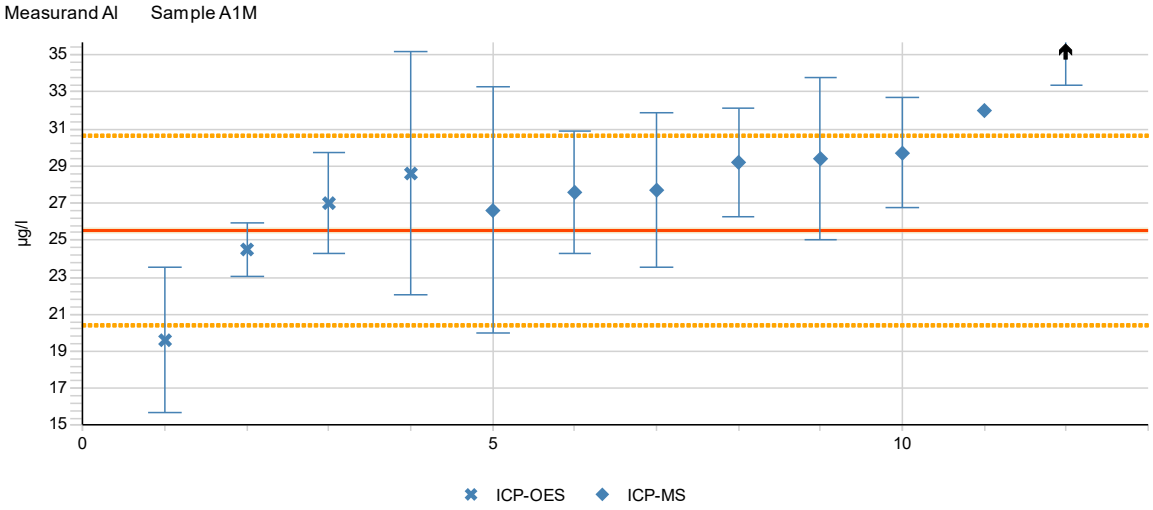
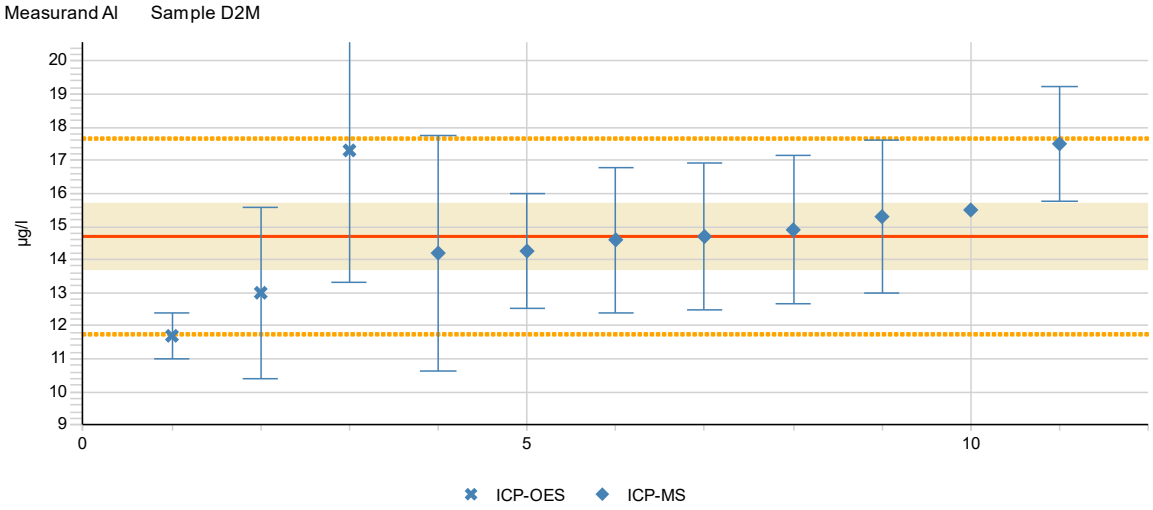


Appendix 10. Results grouped according to the methods

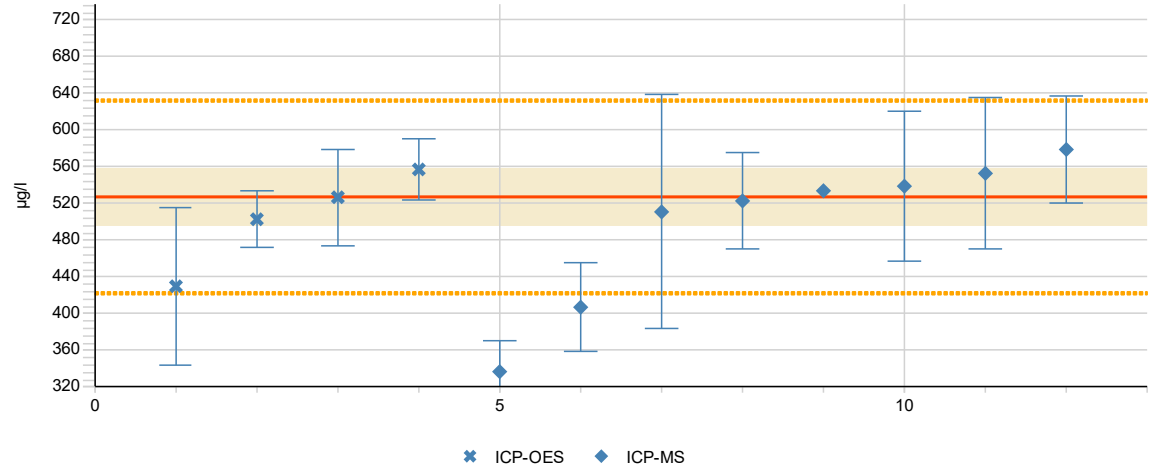
In figures:

- The dashed lines describe the standard deviation for the proficiency assessment, the red solid line shows the assigned value, the shaded area describes the expanded uncertainty of the assigned value, and the arrow describes the value outside the scale.

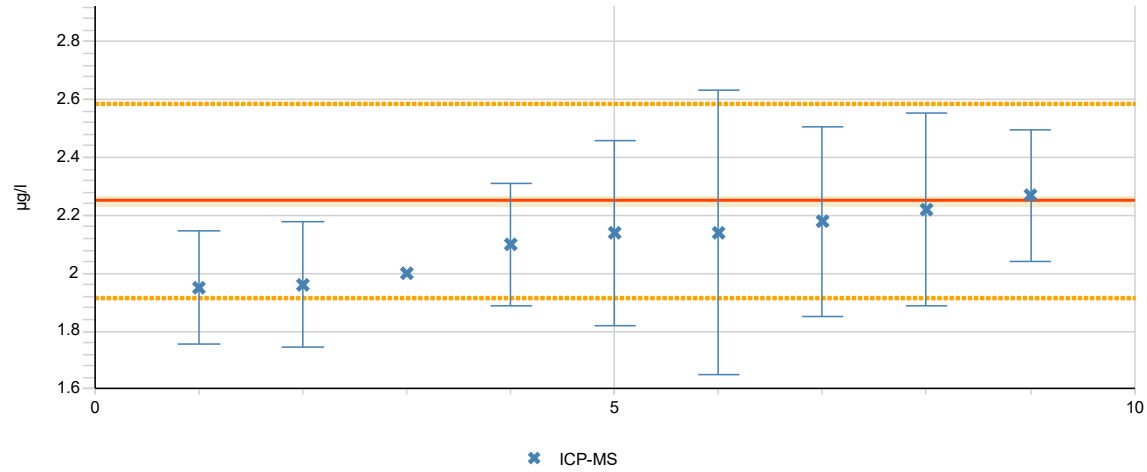




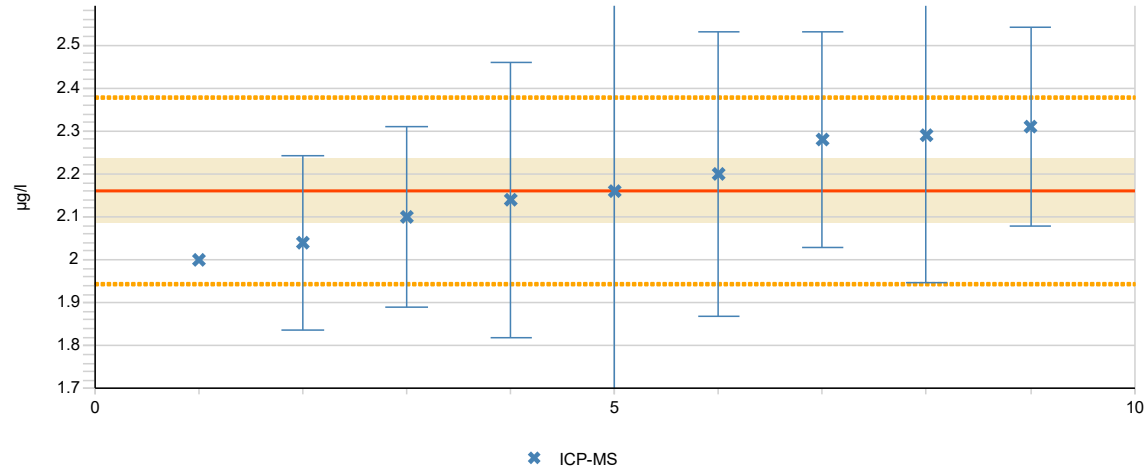
Measurand Al Sample N3M



Measurand As Sample A1M



Measurand As Sample D2M



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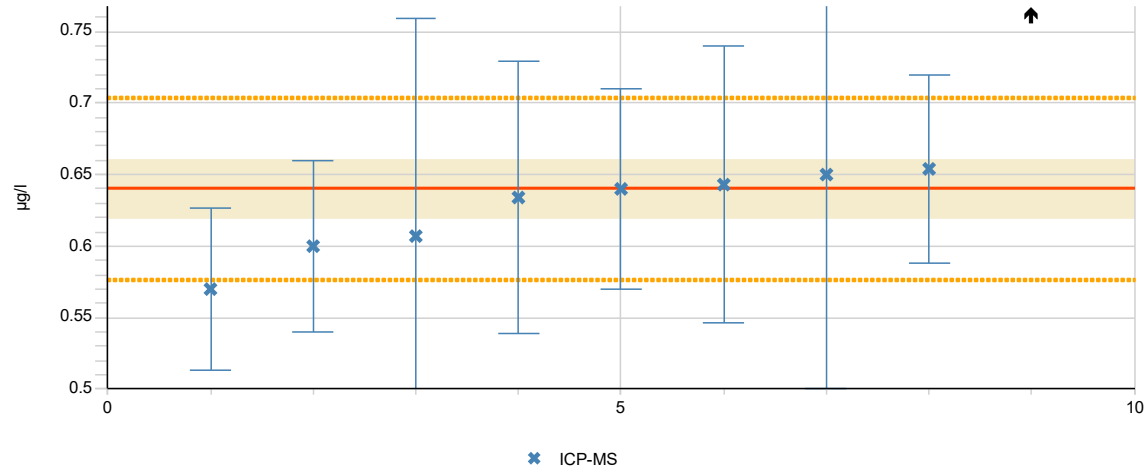
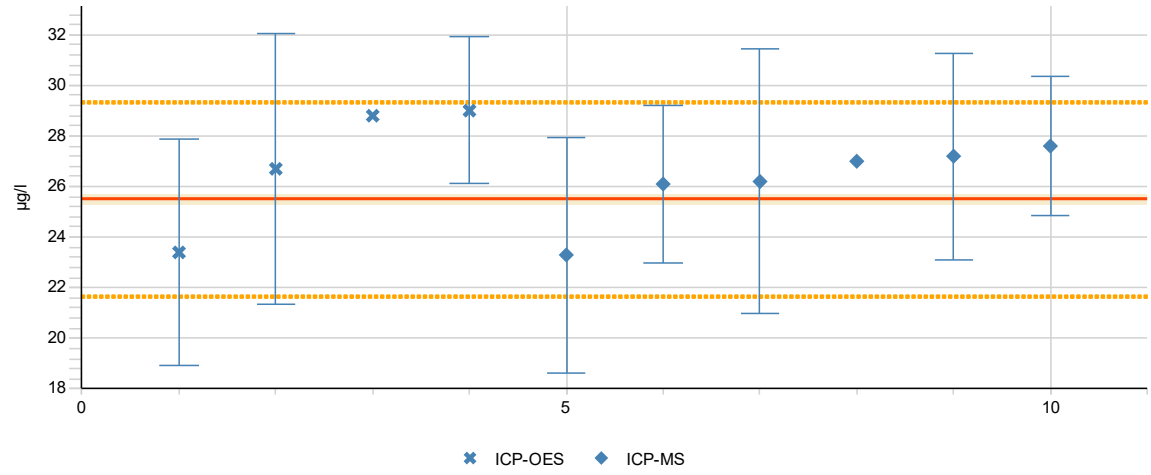
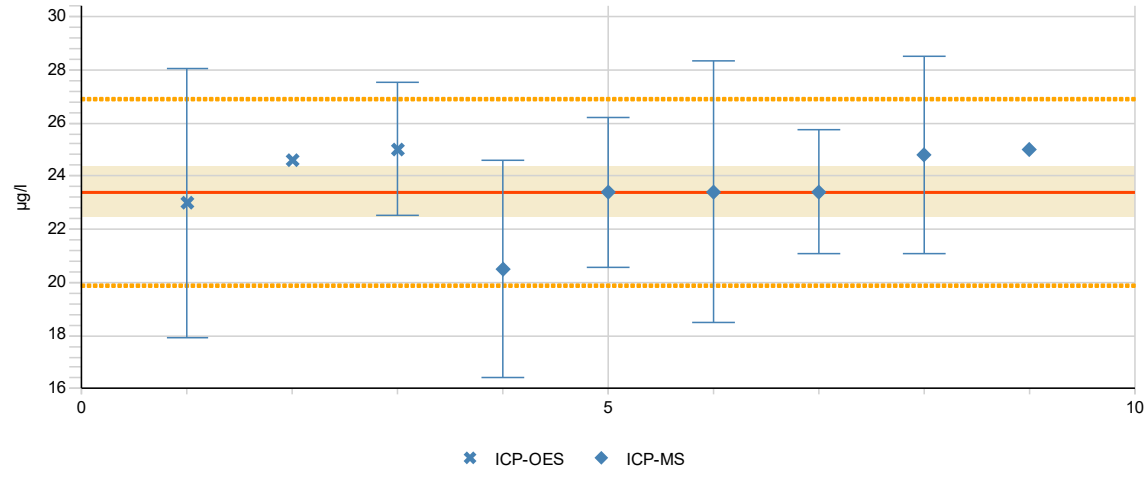


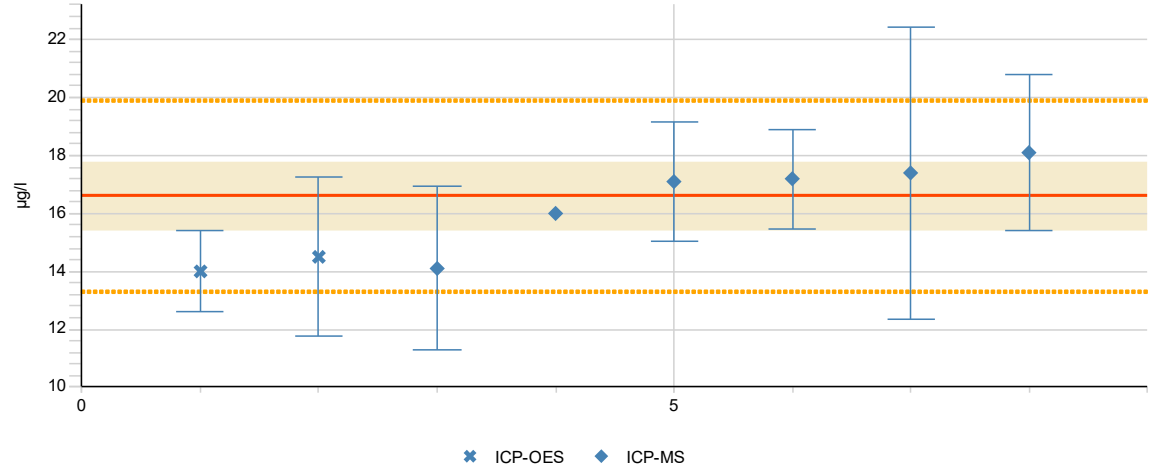
Measurand B Sample A1M



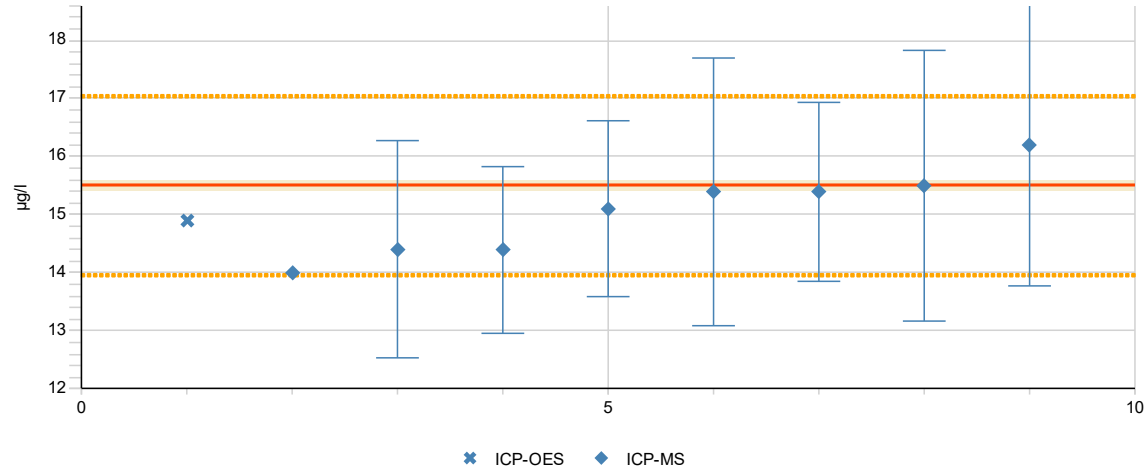
Measurand B Sample D2M



Measurand B Sample N3M



Measurand Ba Sample A1M



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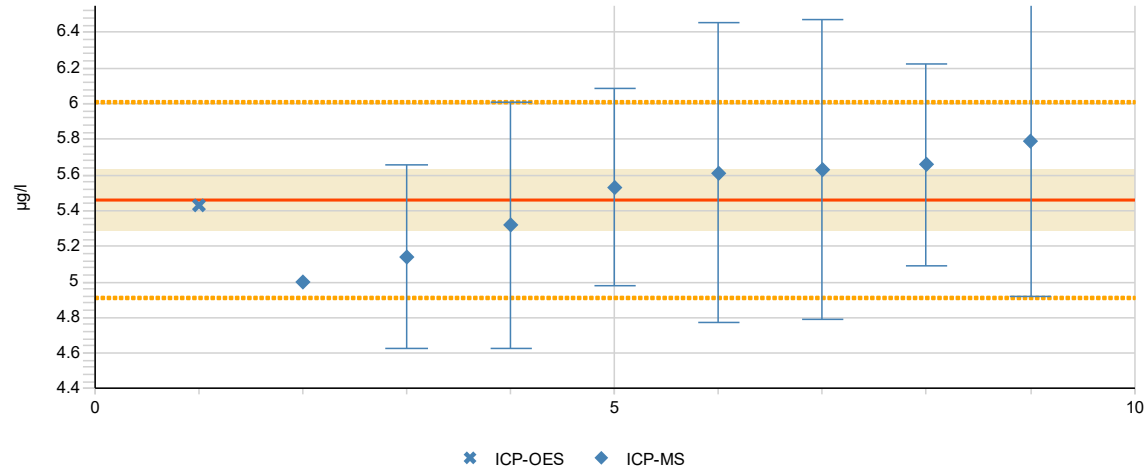

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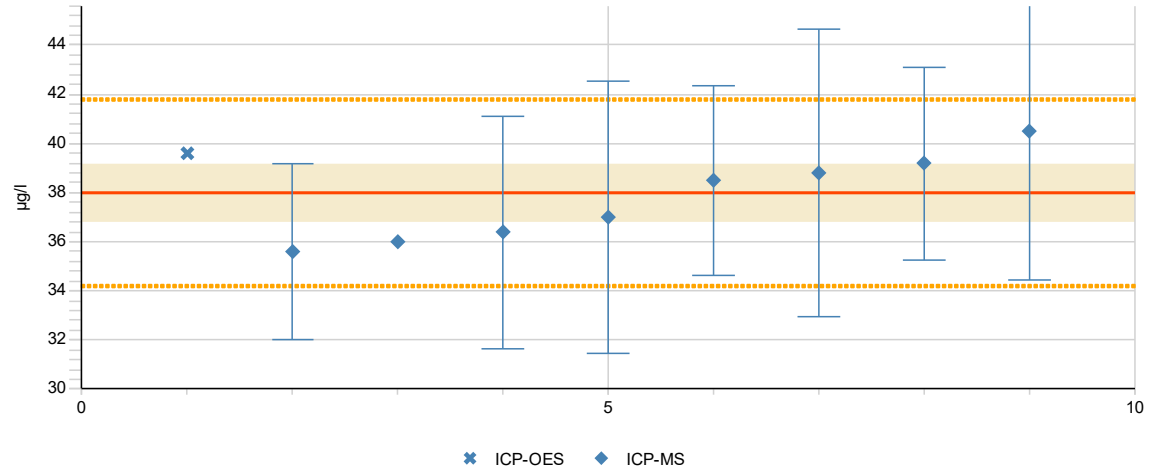
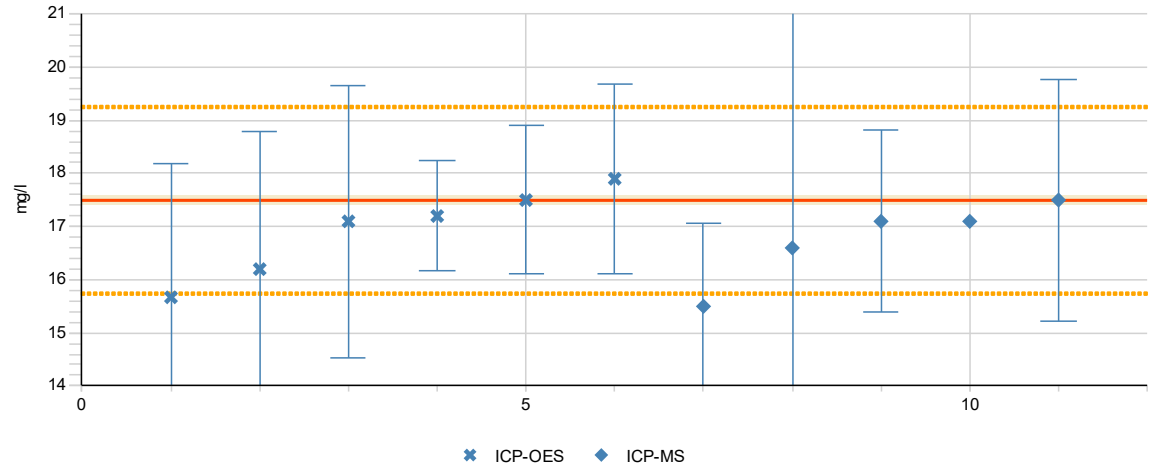


Measurand Ca Sample A1M



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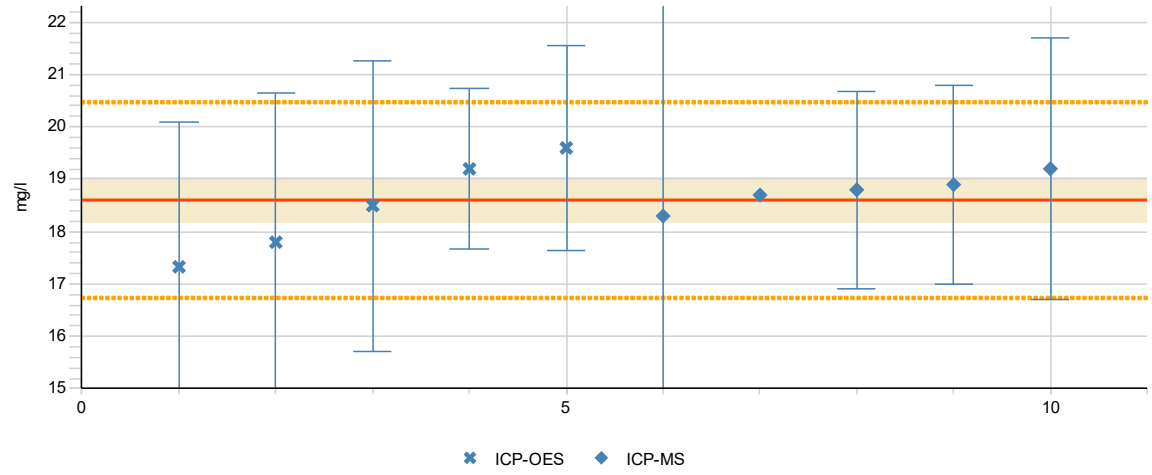

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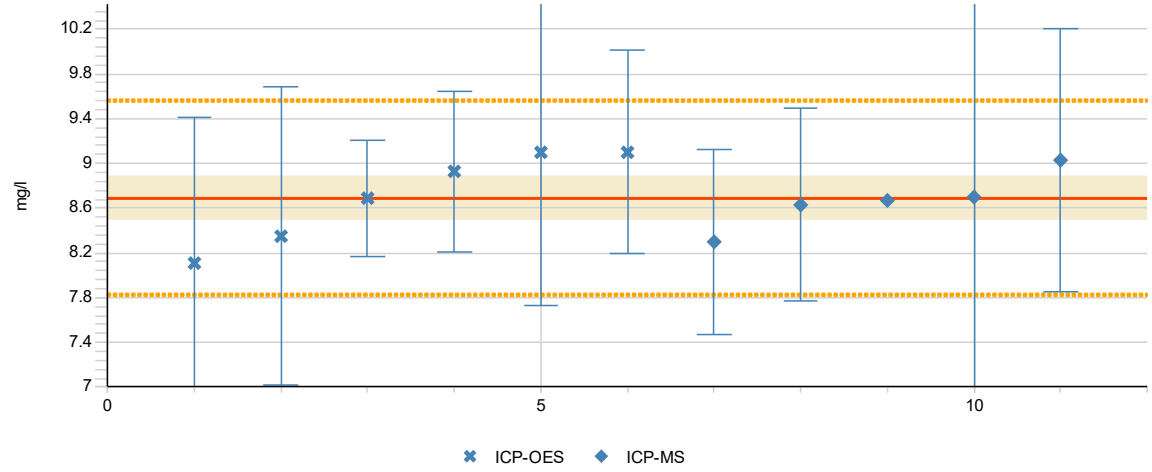
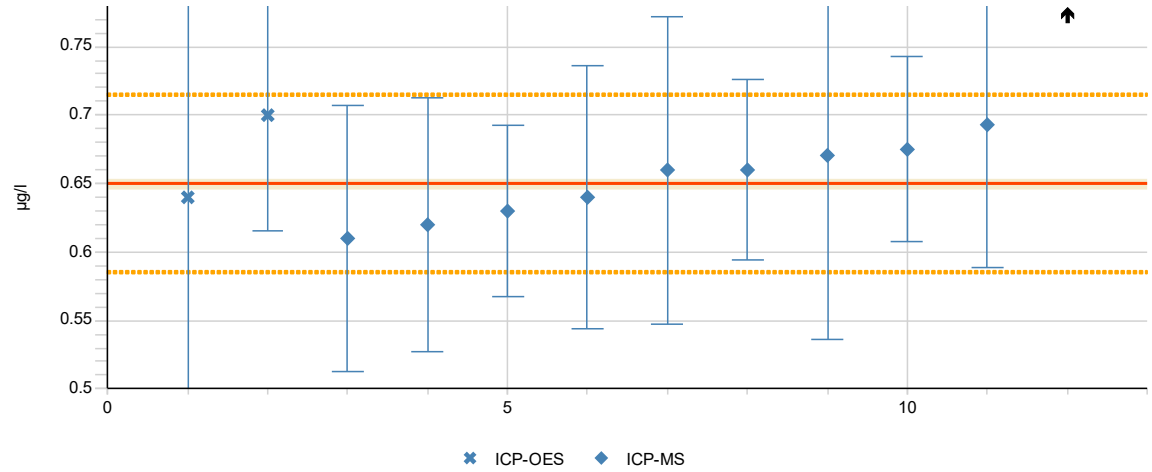
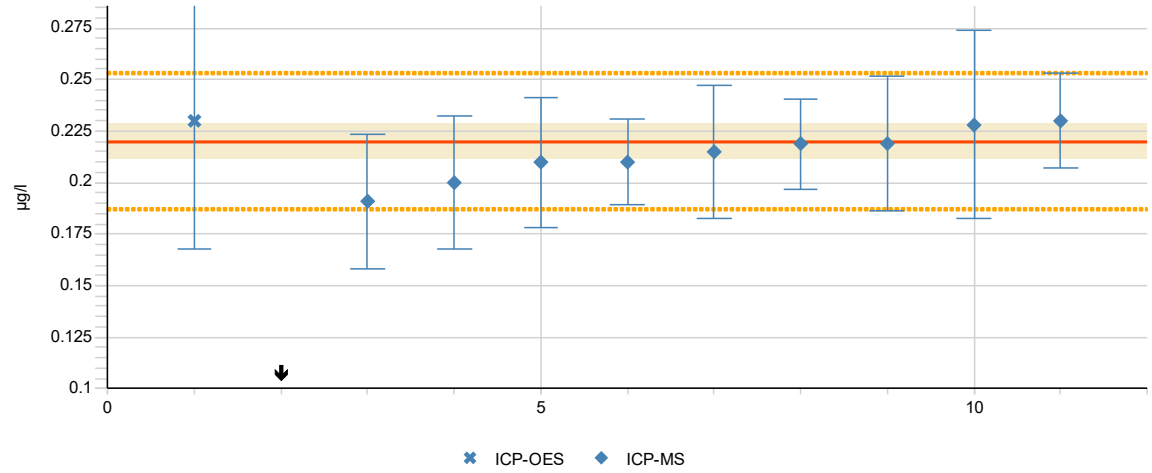


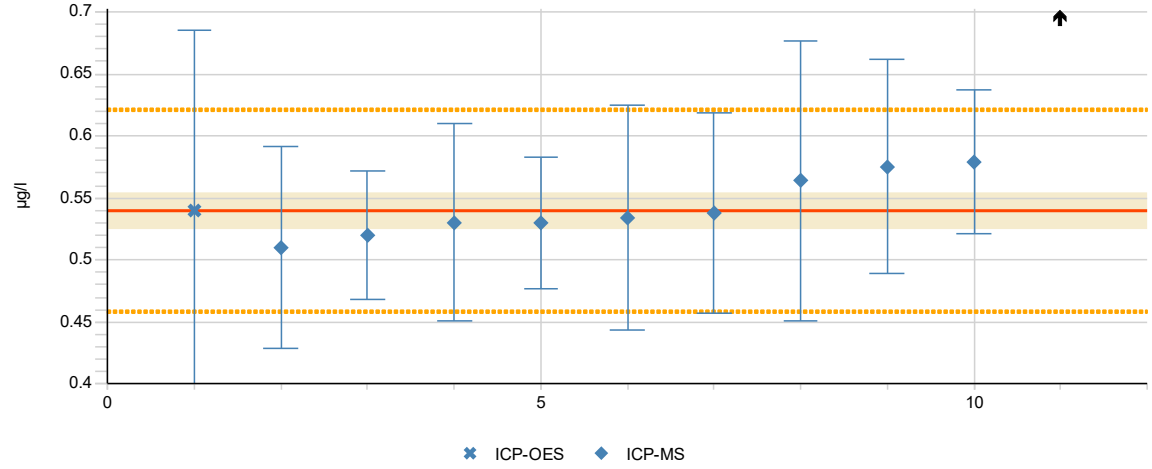
Measurand Cd Sample A1M



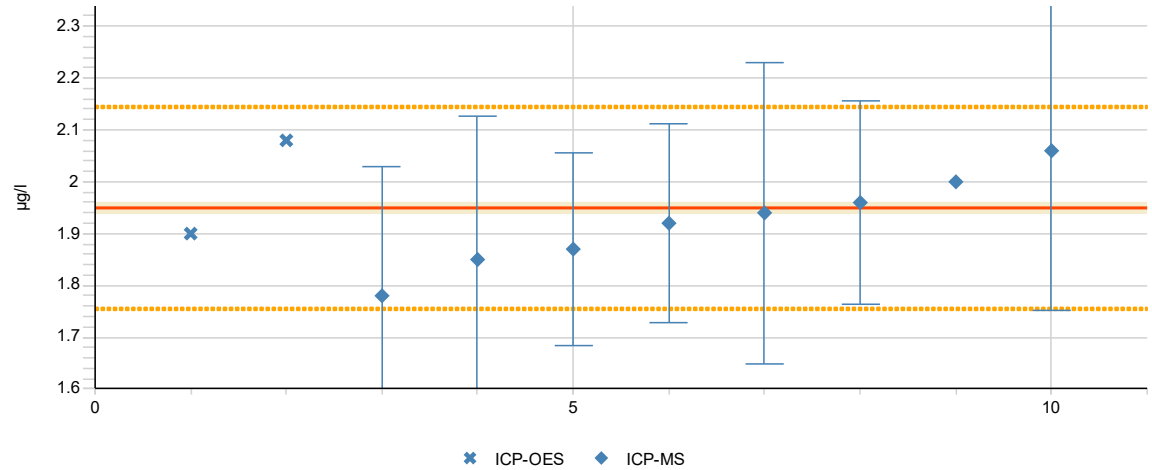
Measurand Cd Sample D2M



Measurand Cd Sample N3M



Measurand Co Sample A1M



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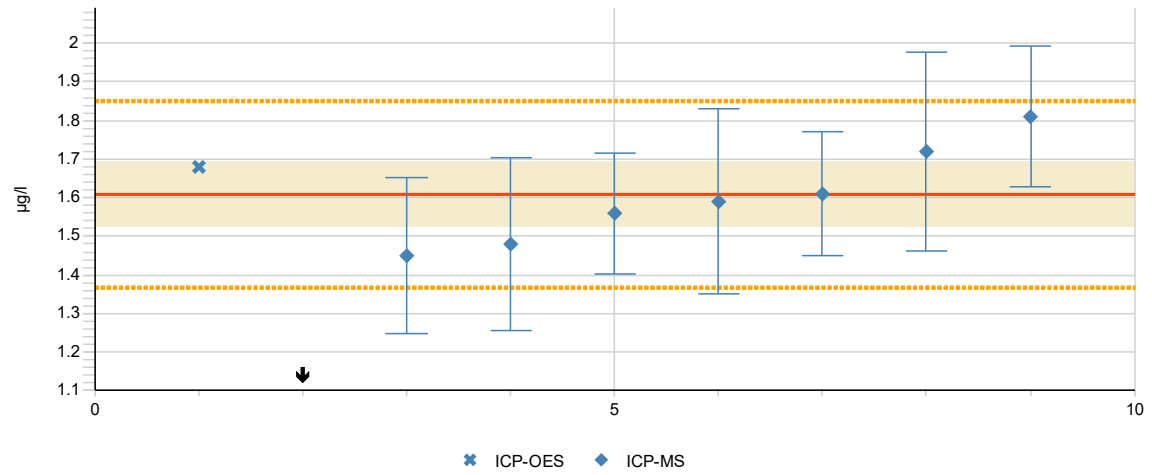

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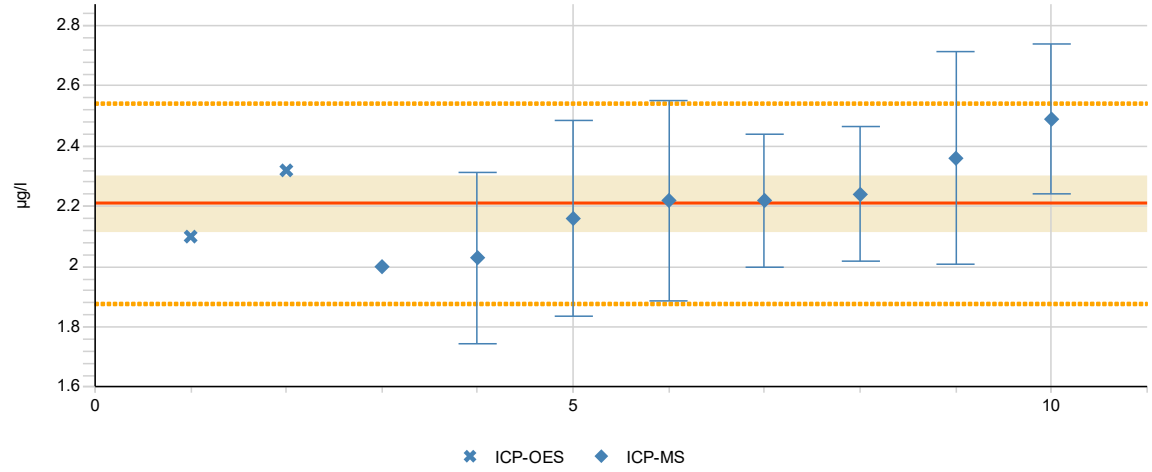
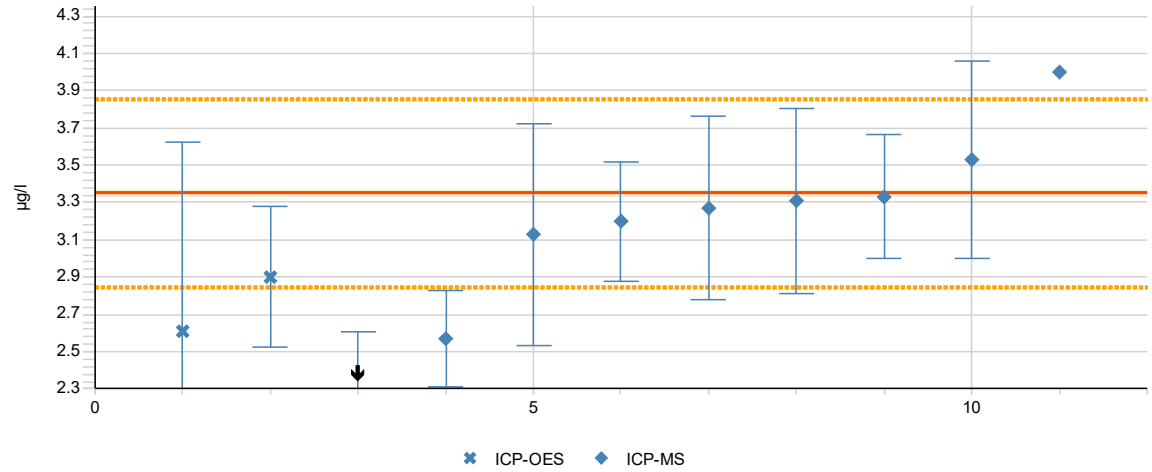
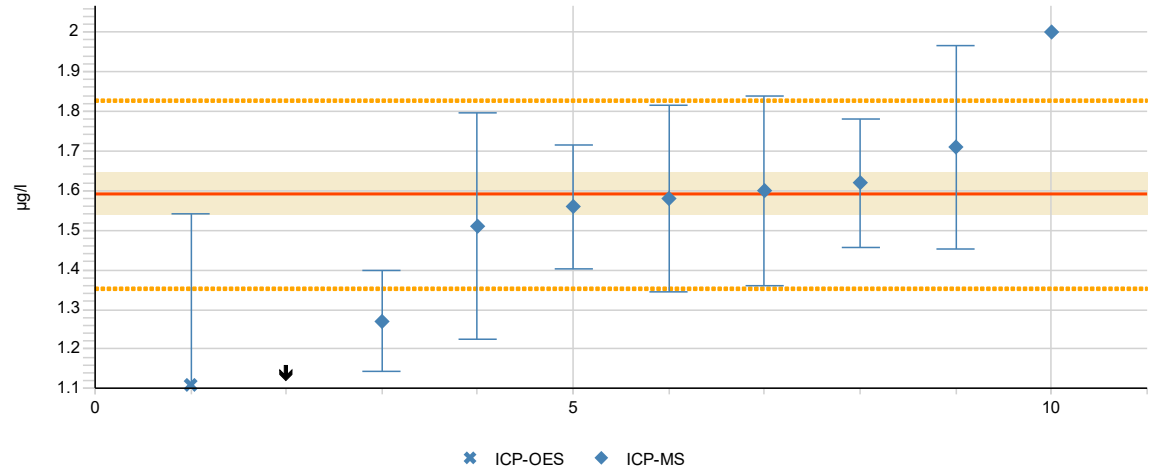
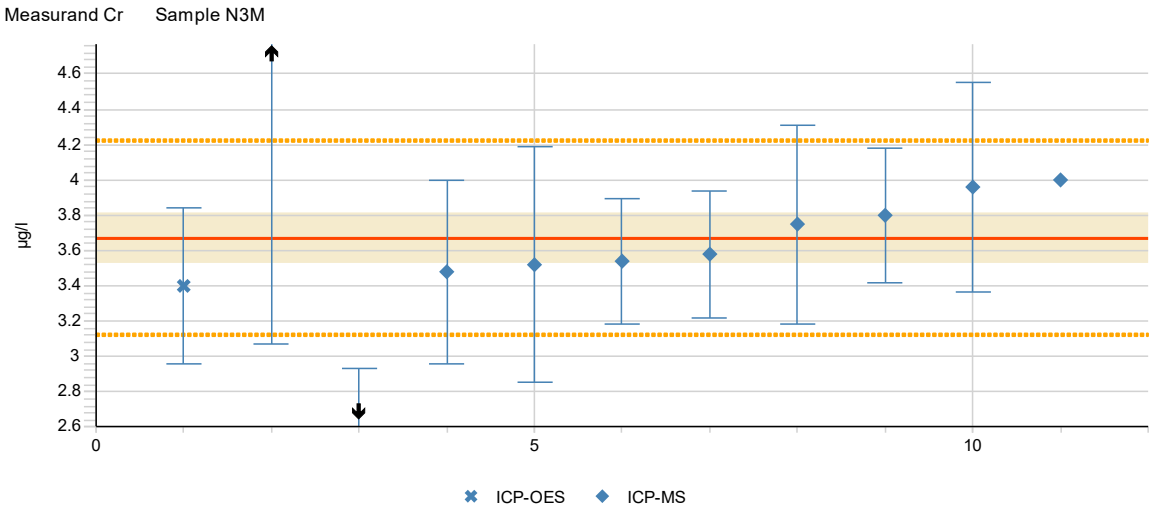


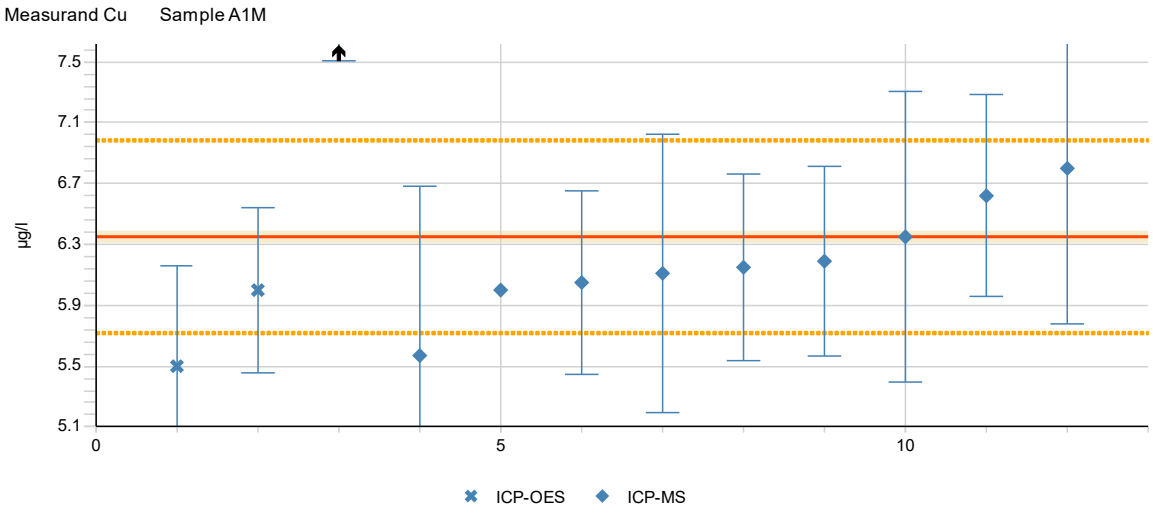
Measurand Cr Sample A1M

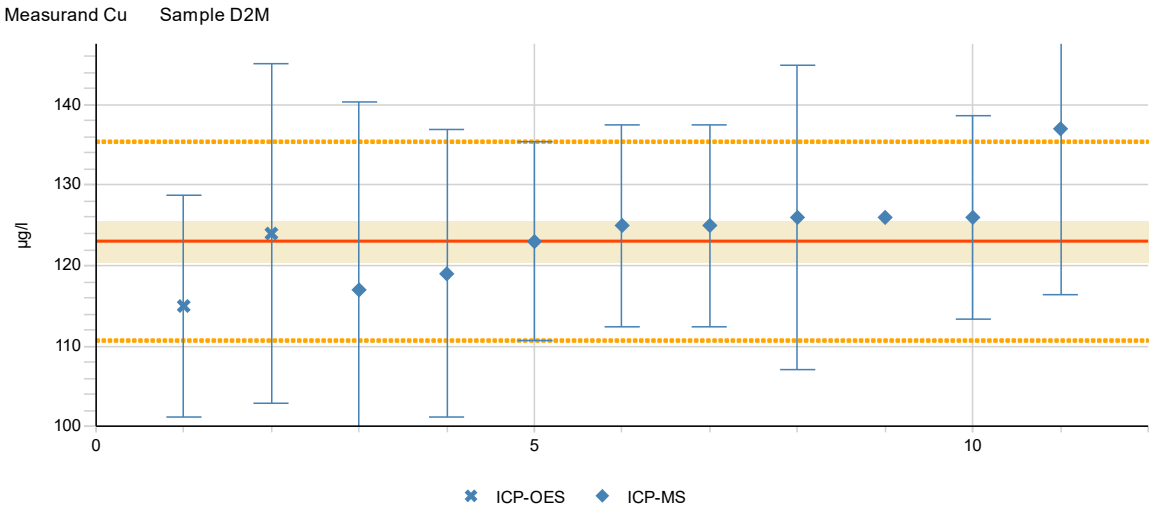


Measurand Cr Sample D2M

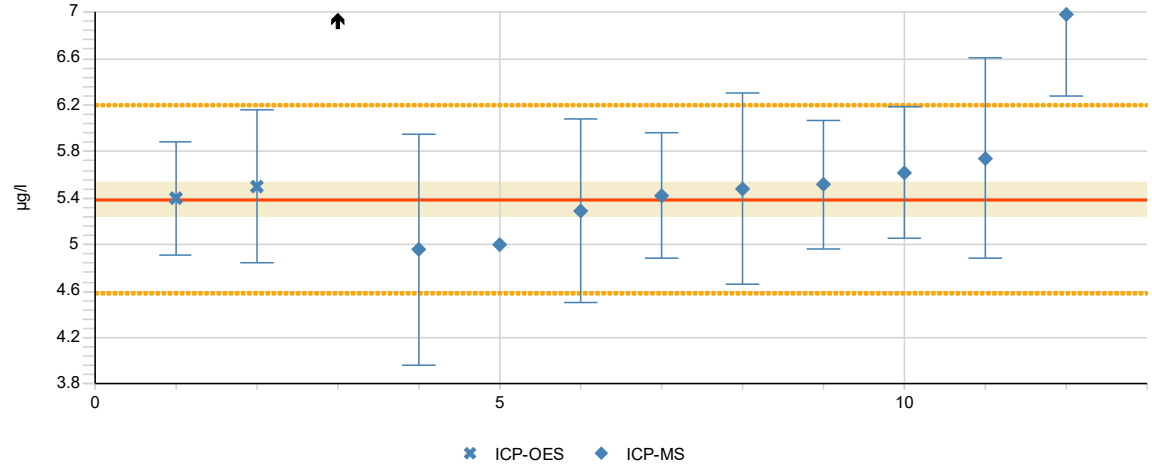



Measurand Cr Sample N3M
µg/l
4.6
4.4
4.2
4
3.8
3.6
3.4
3.2
3
2.8
2.6
0
5
10
ICP-OES
ICP-MS

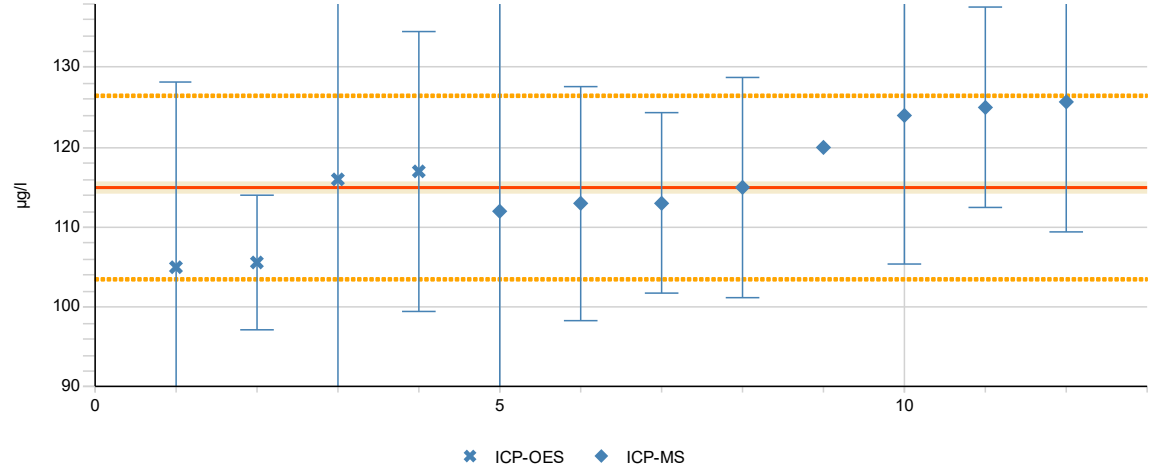

Measurand Cu Sample A1M
µg/l
7.5
7.1
6.7
6.3
5.9
5.5
5.1
0
5
10
ICP-OES
ICP-MS


Measurand Cu Sample D2M
µg/l
140
130
120
110
100
0
5
10
ICP-OES
ICP-MS

Measurand Cu Sample N3M



Measurand Fe Sample A1M



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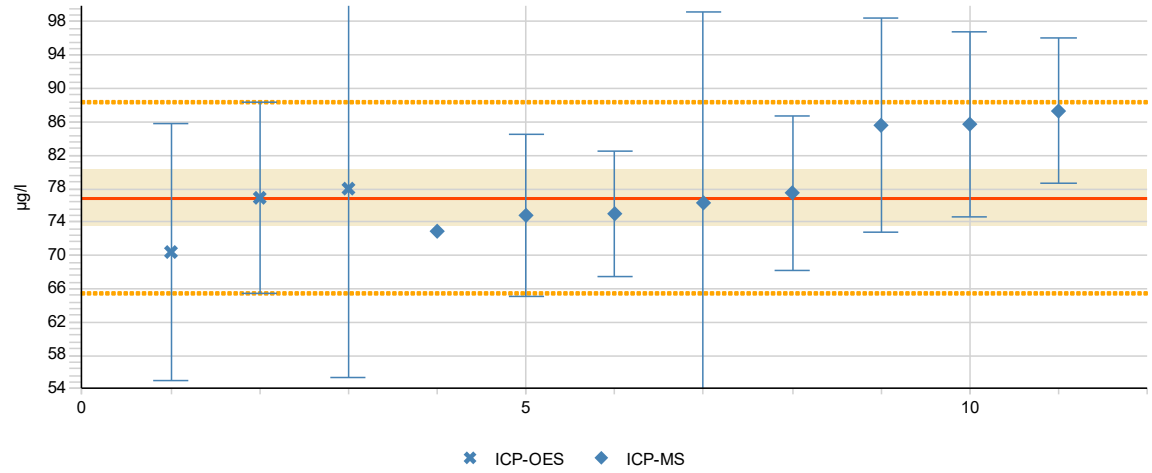
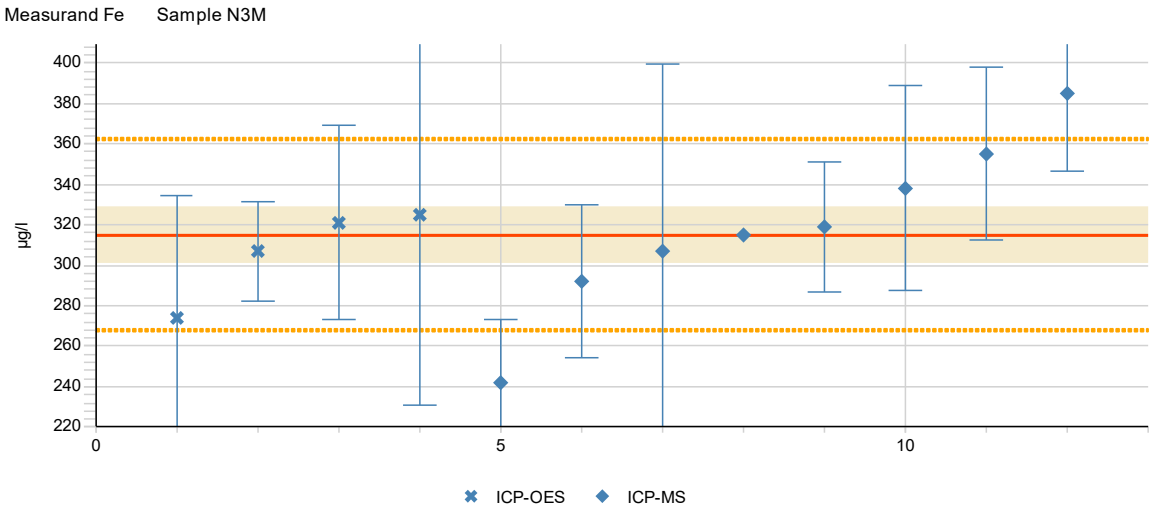
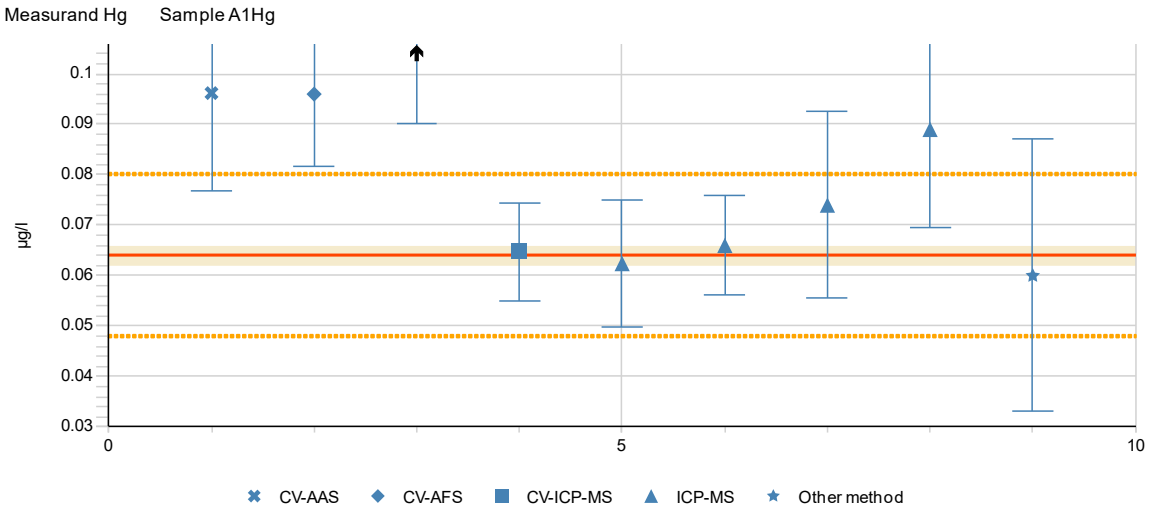
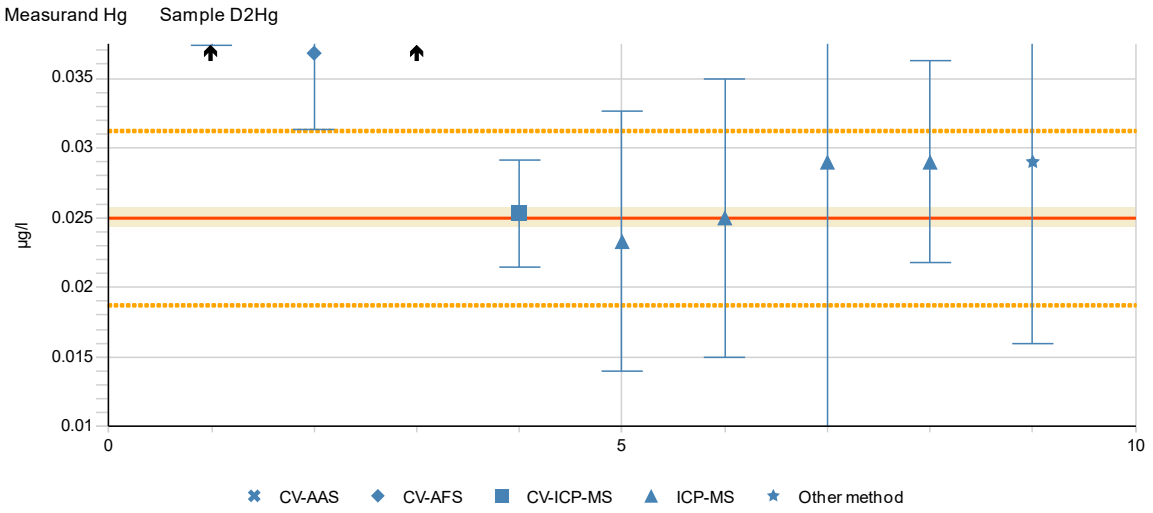
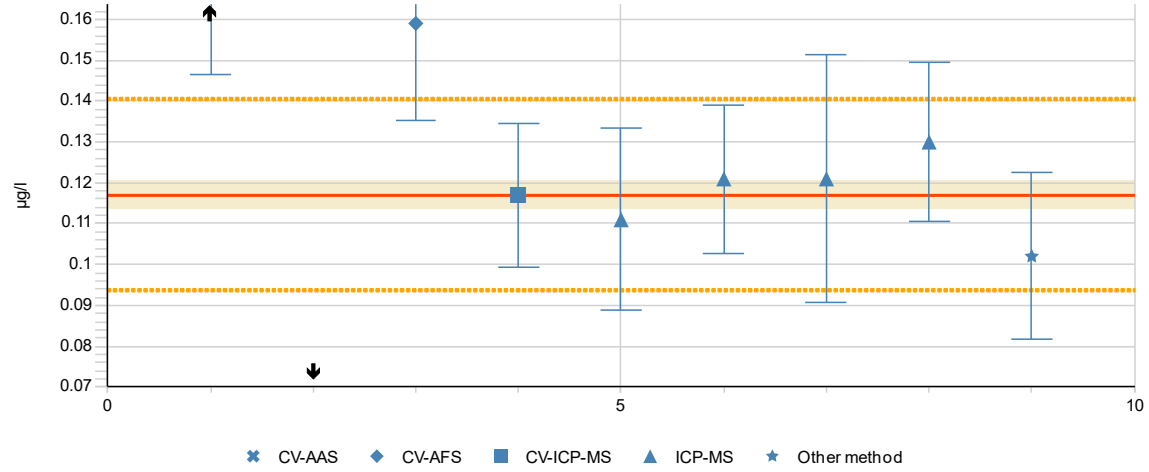



Measurand Fe Sample N3M
µg/l
400
380
360
340
320
300
280
260
240
220
0
5
10
ICP-OES
ICP-MS

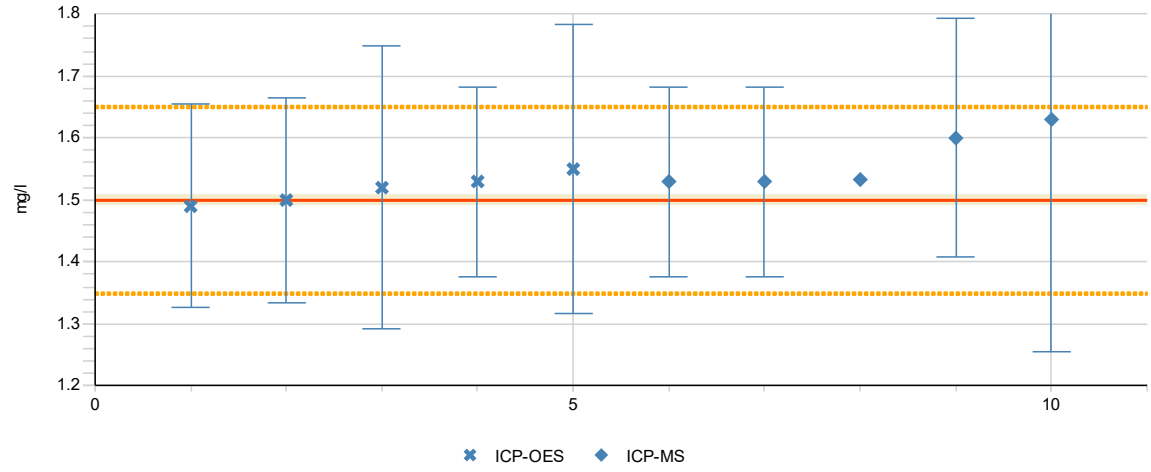

Measurand Hg Sample A1Hg
µg/l
0.1
0.09
0.08
0.07
0.06
0.05
0.04
0.03
0
5
10
CV-AAS
CV-AFS
CV-ICP-MS
ICP-MS
Other method


Measurand Hg Sample D2Hg
µg/l
0.035
0.03
0.025
0.02
0.015
0.01
0
5
10
CV-AAS
CV-AFS
CV-ICP-MS
ICP-MS
Other method

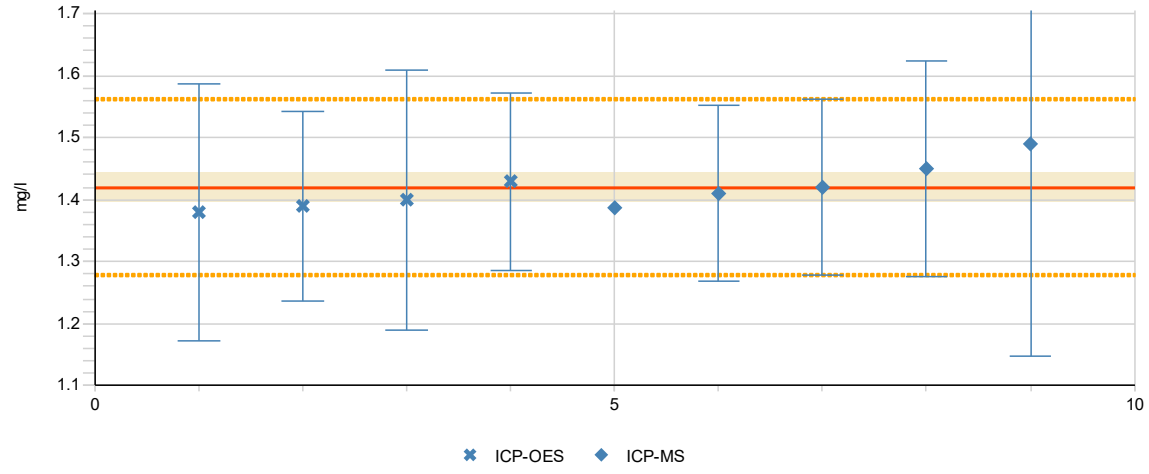
Measurand Hg Sample N3Hg



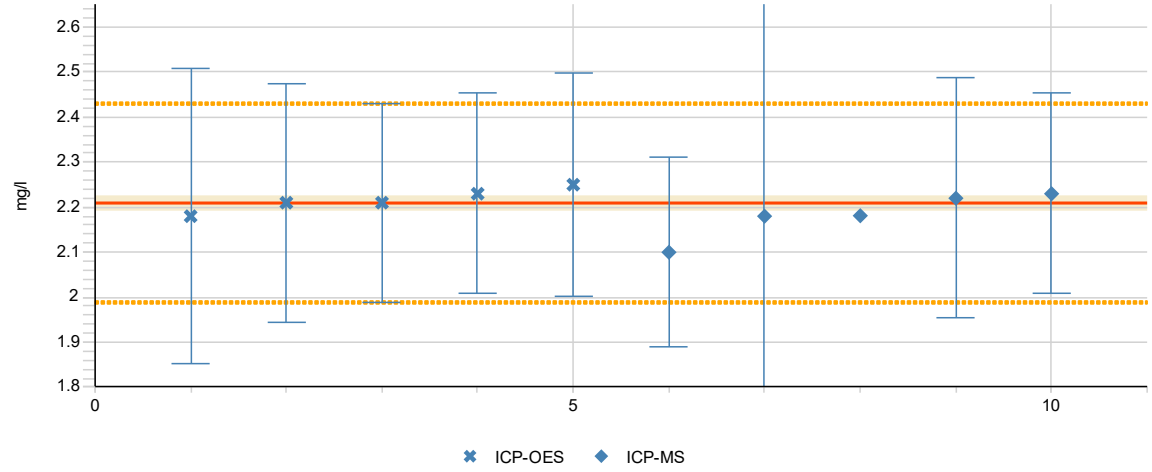
Measurand K Sample A1M



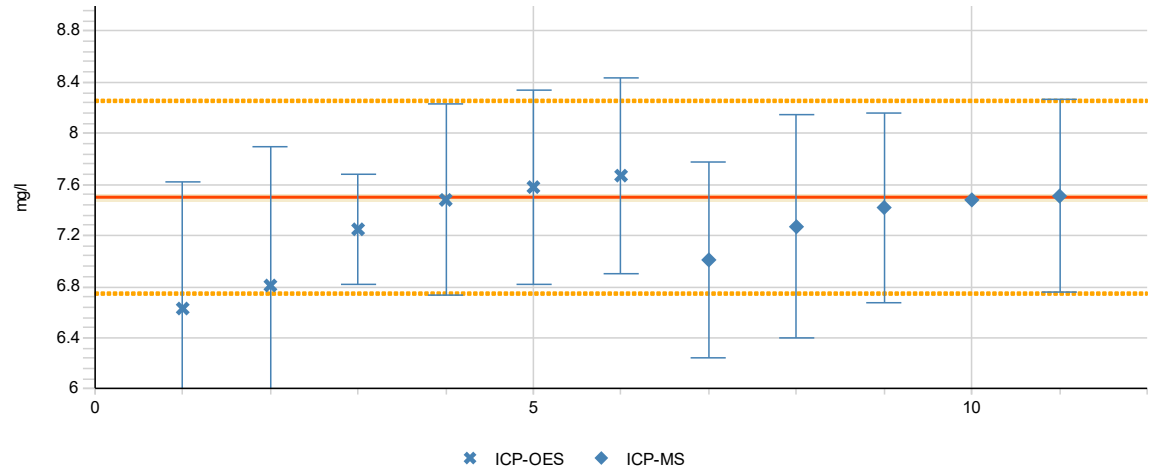
Measurand K Sample D2M



Measurand K Sample N3M



Measurand Mg Sample A1M



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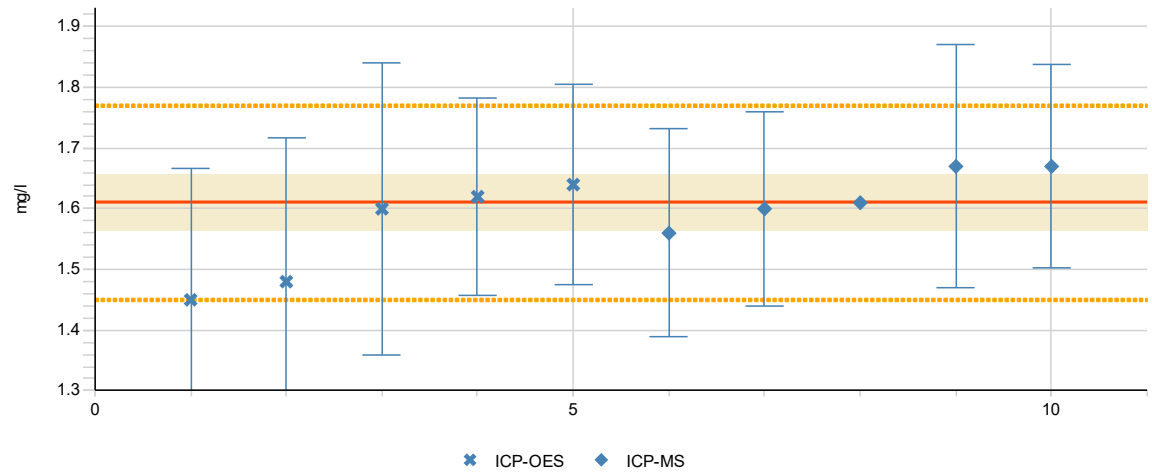

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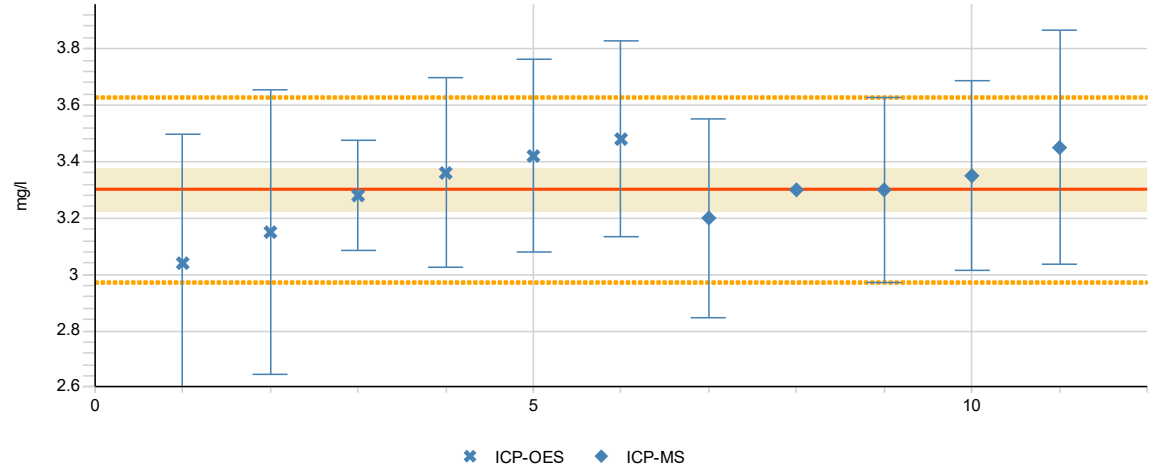
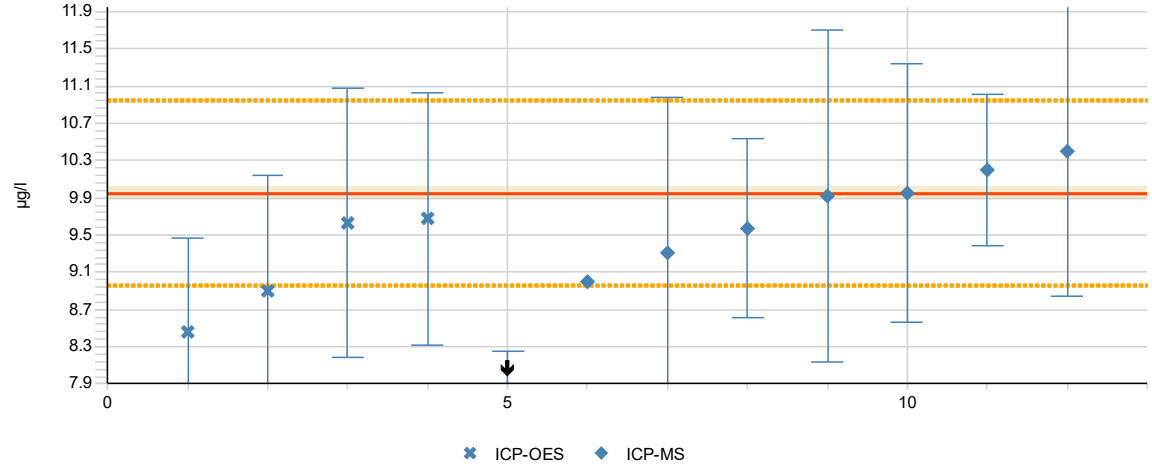
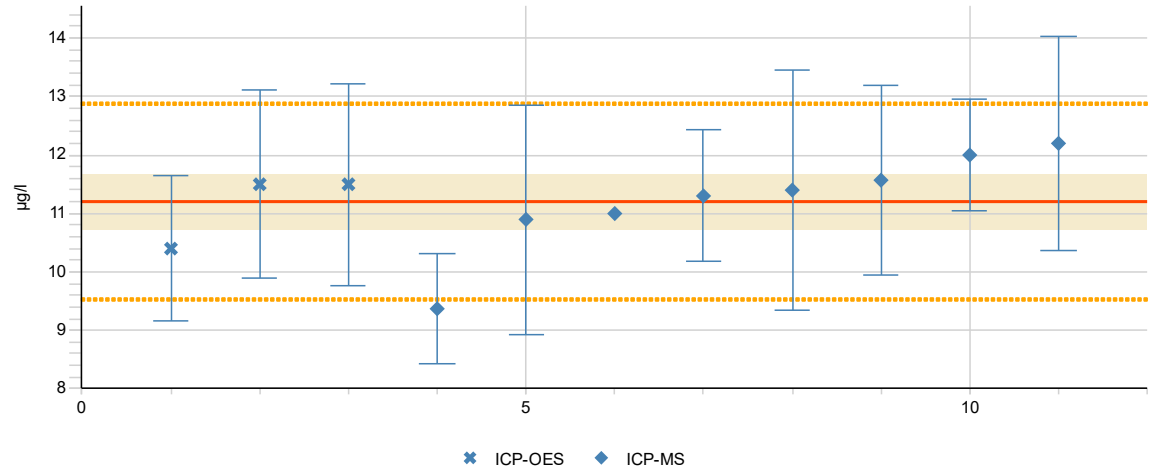


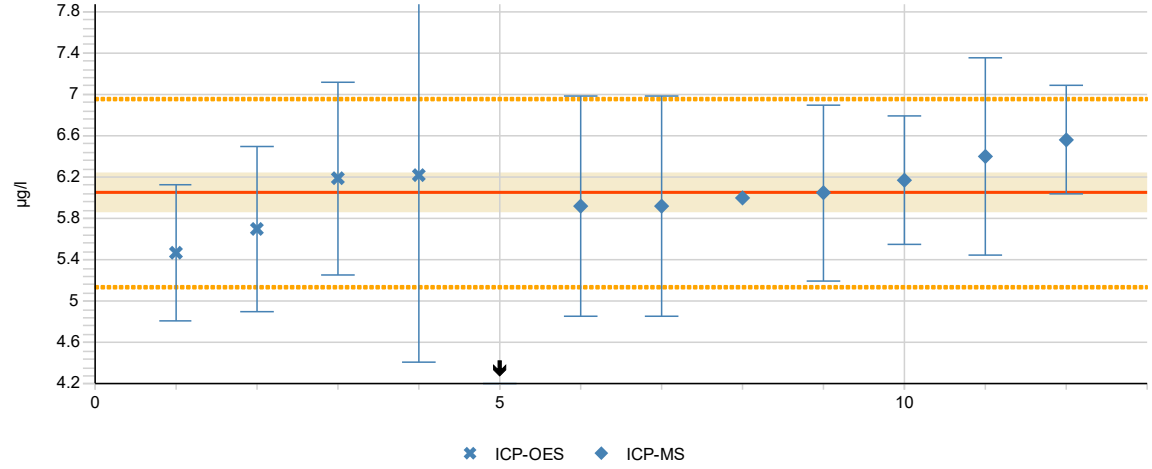
Measurand Mn Sample A1M



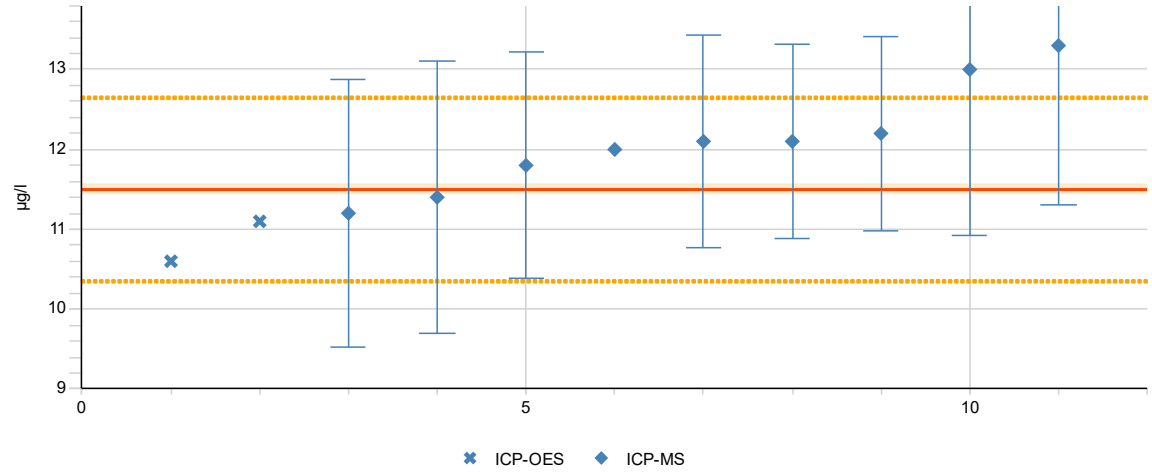
Measurand Mn Sample D2M



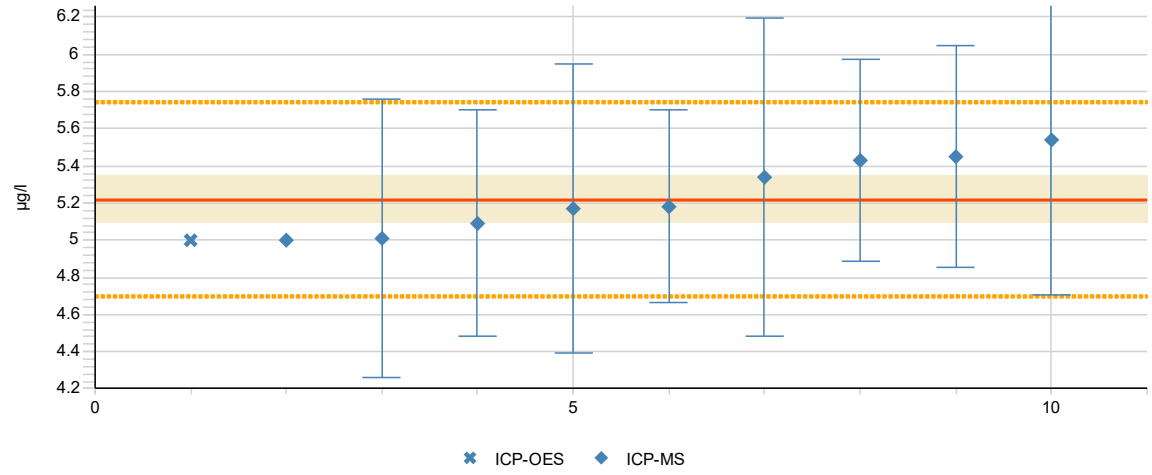
Measurand Mn Sample N3M



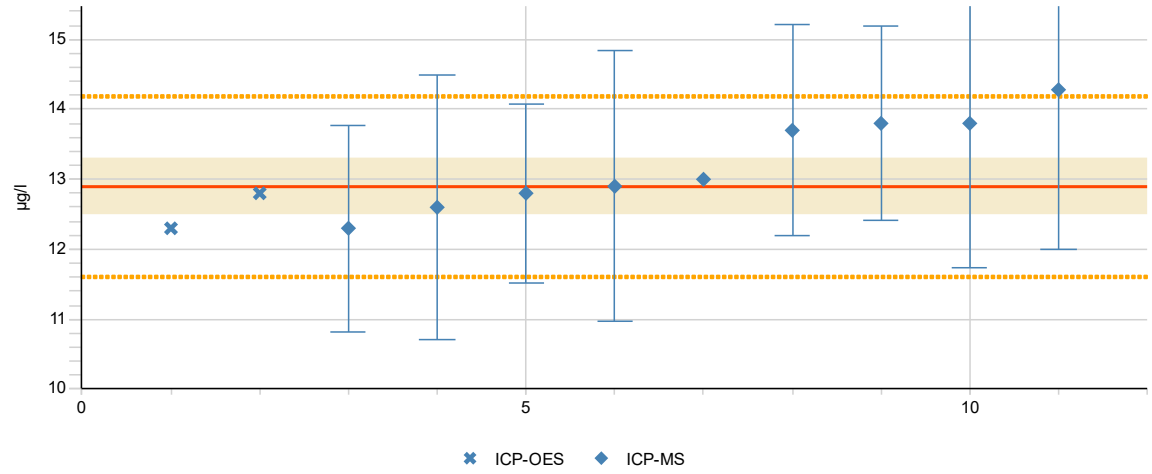
Measurand Mo Sample A1M



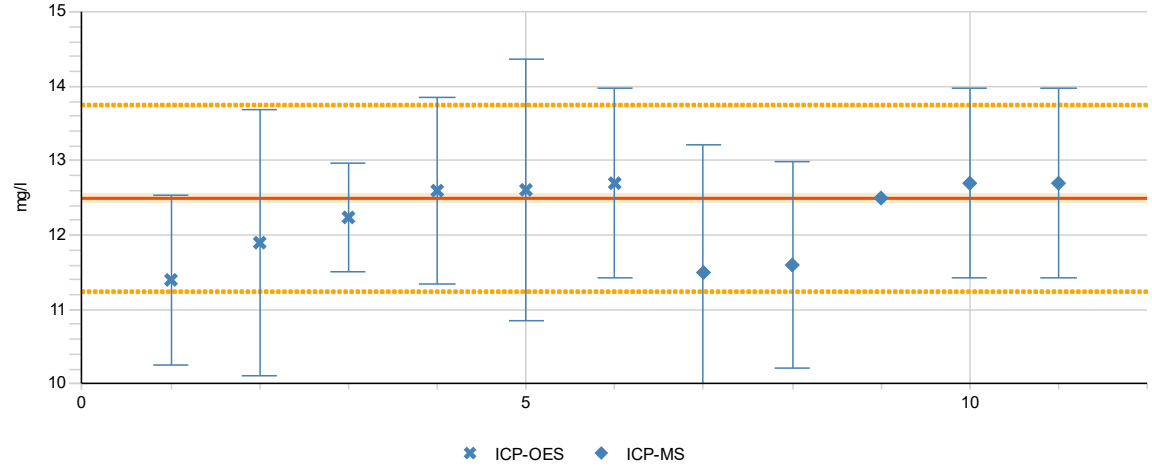
Measurand Mo Sample D2M



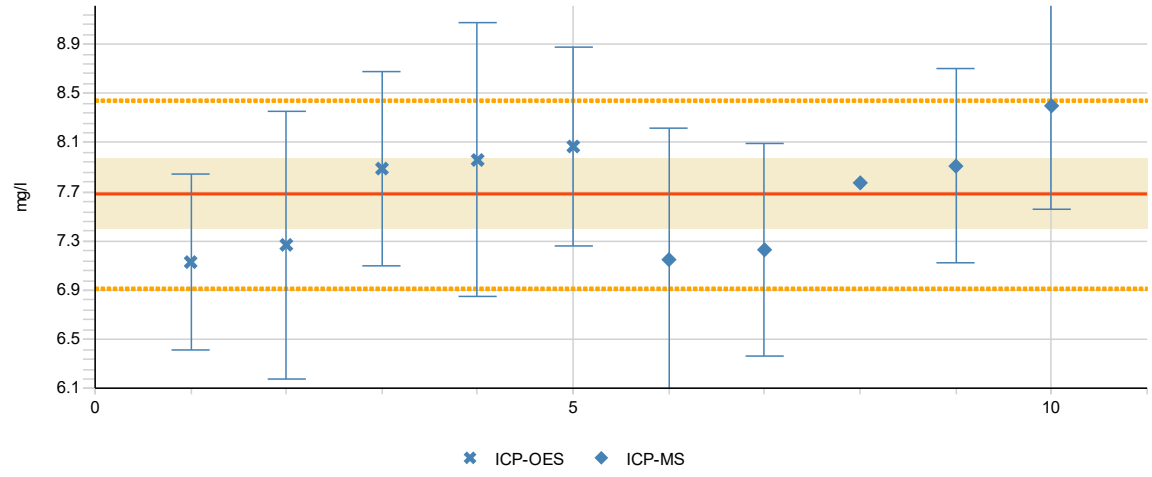
Measurand Mo Sample N3M



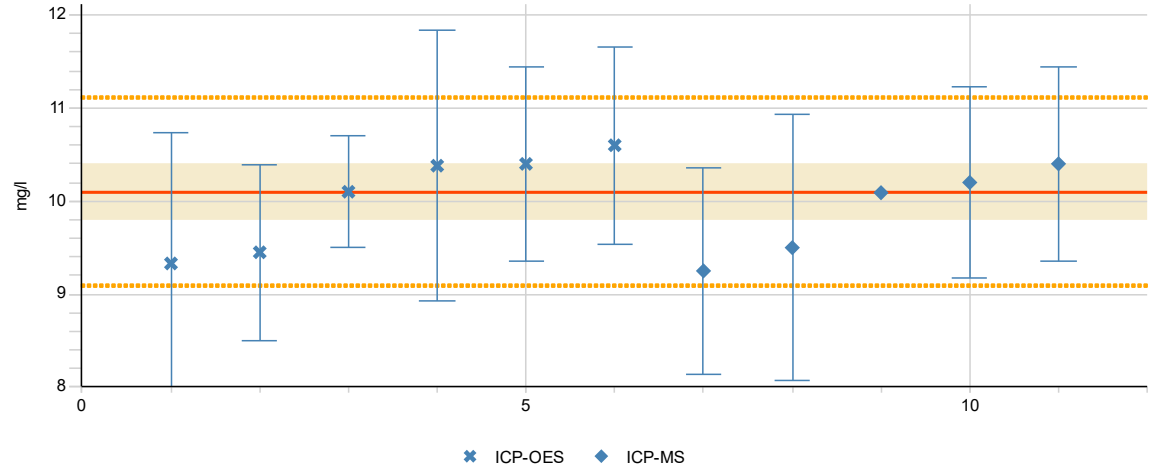
Measurand Na Sample A1M



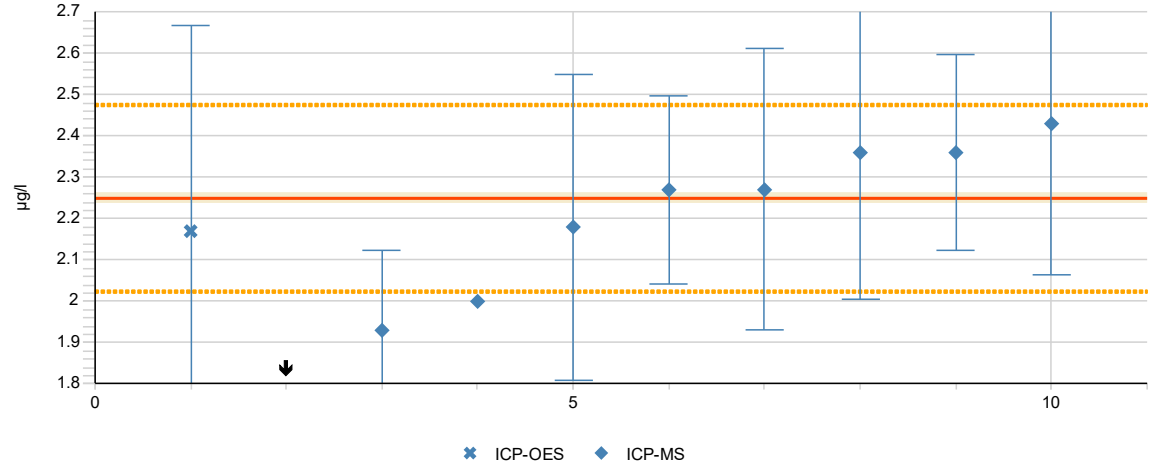
Measurand Na Sample D2M



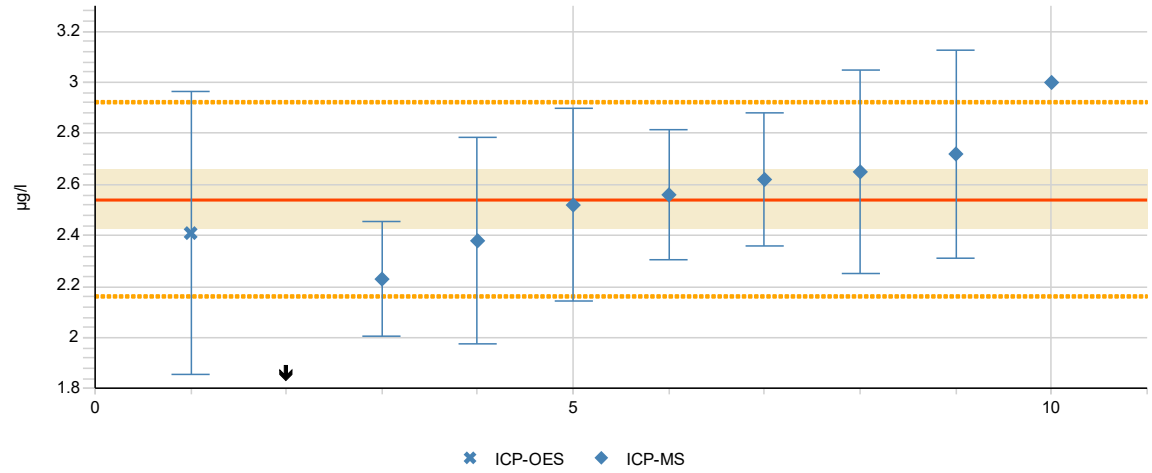
Measurand Na Sample N3M



Measurand Ni Sample A1M



Measurand Ni Sample D2M



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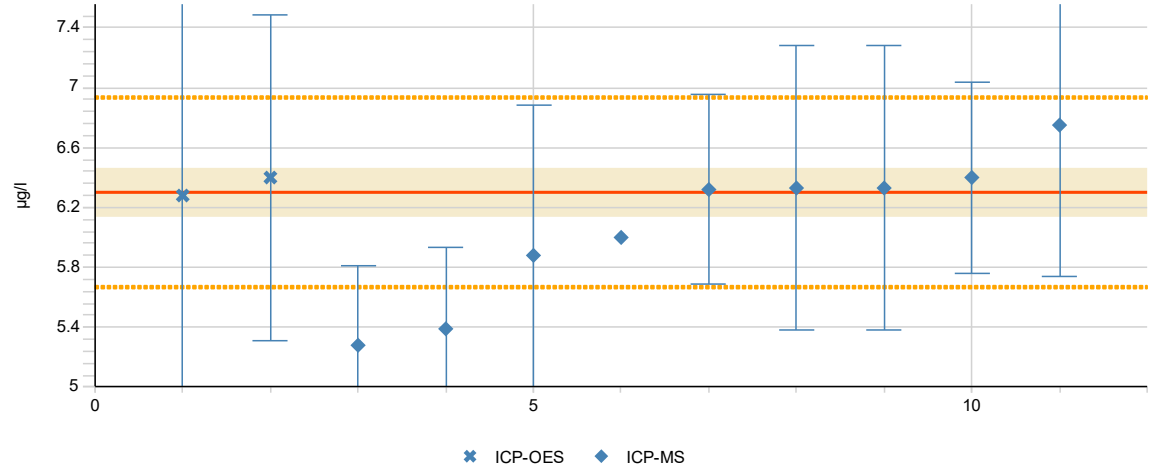
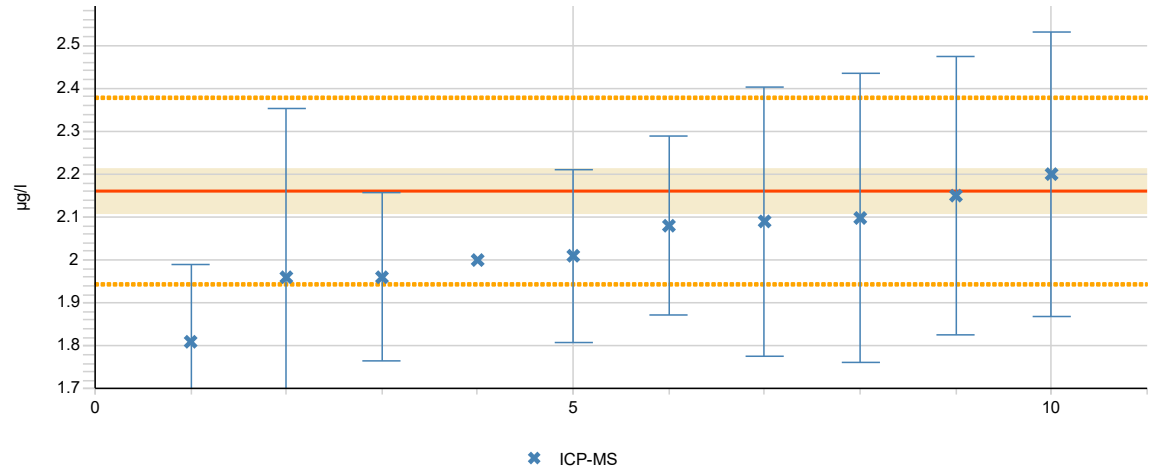
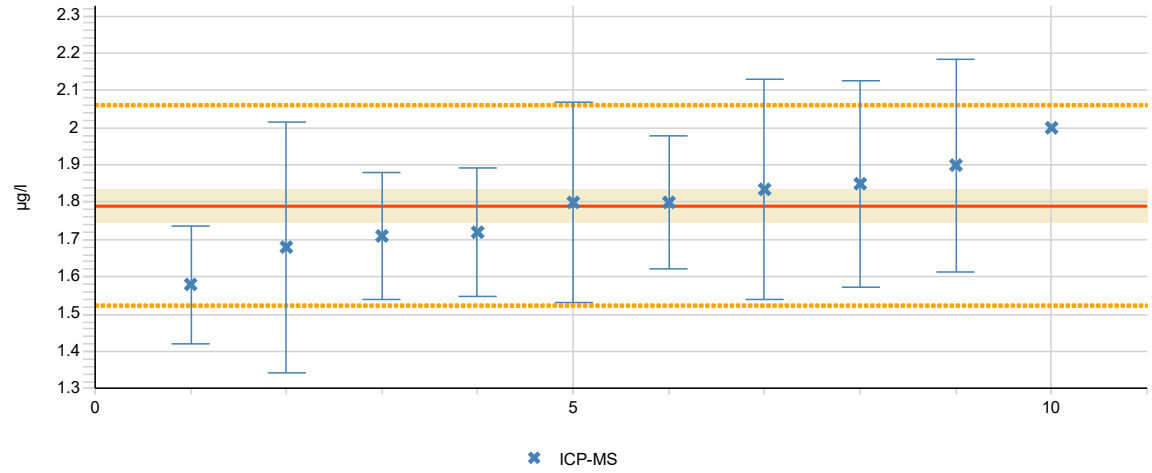


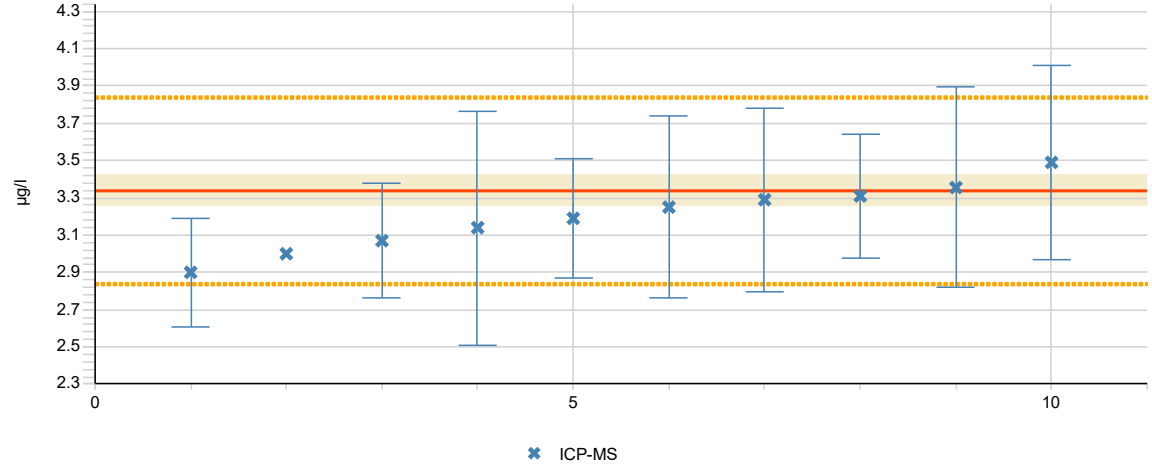
Measurand Pb Sample A1M



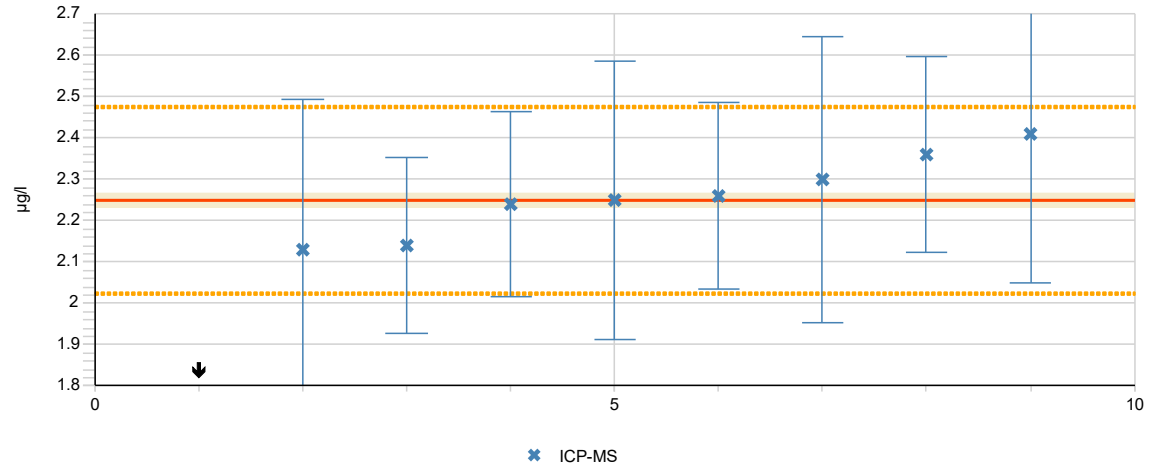
Measurand Pb Sample D2M



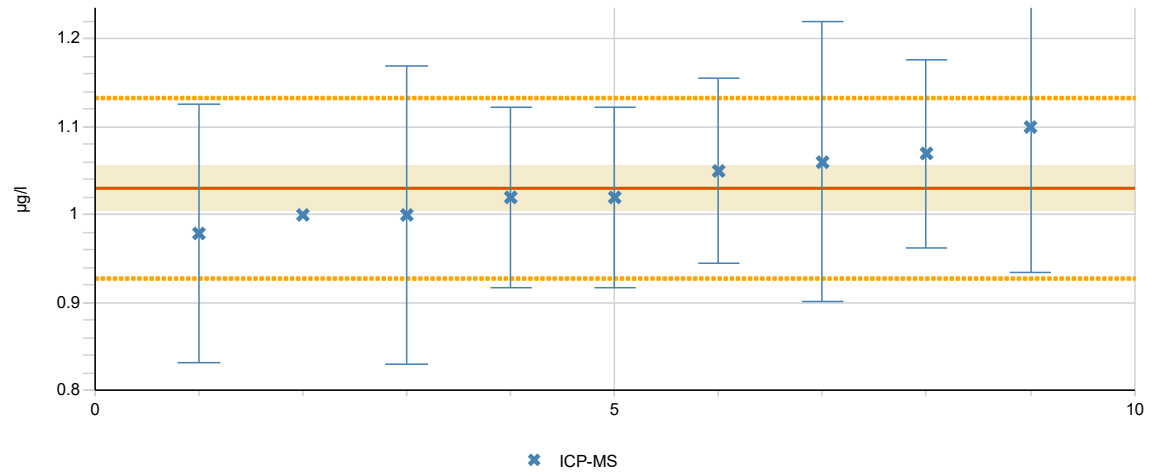
Measurand Pb Sample N3M



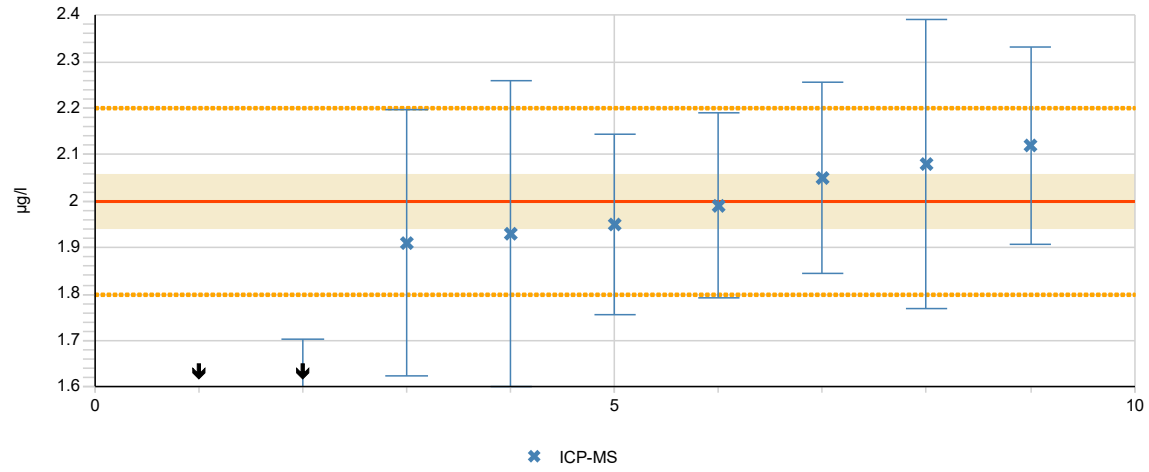
Measurand Sb Sample A1M



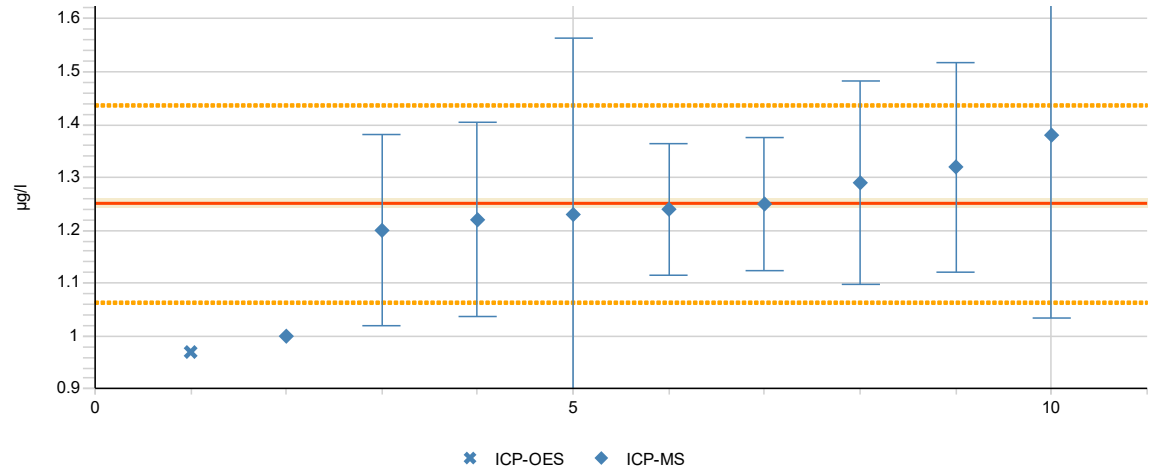
Measurand Sb Sample D2M



Measurand Sb Sample N3M



Measurand Se Sample A1M



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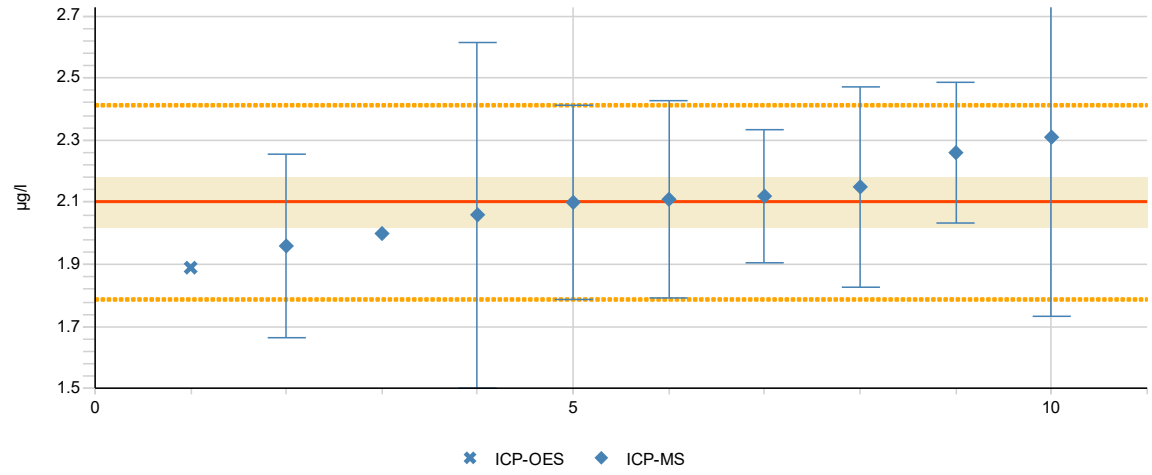
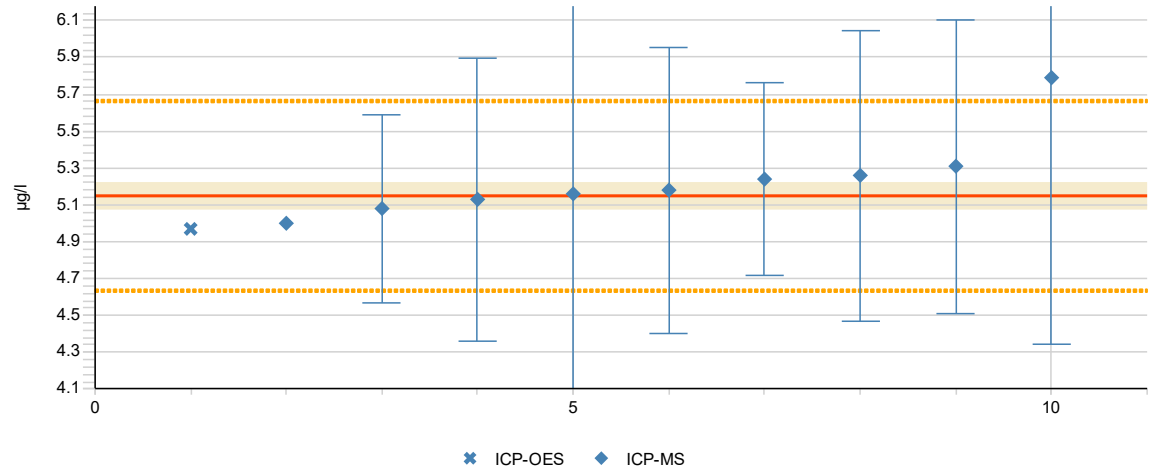
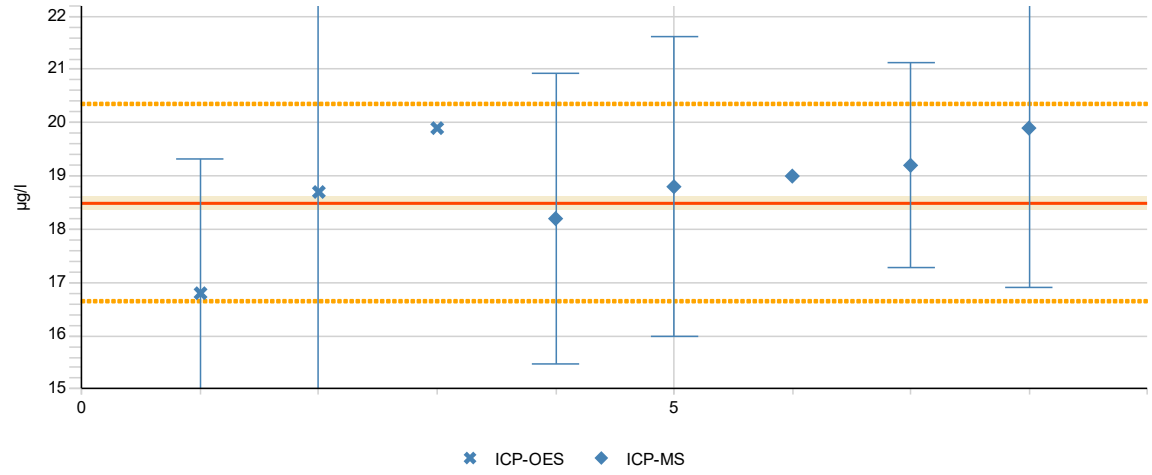


Measurand Se Sample N3M



Measurand Ti Sample A1M



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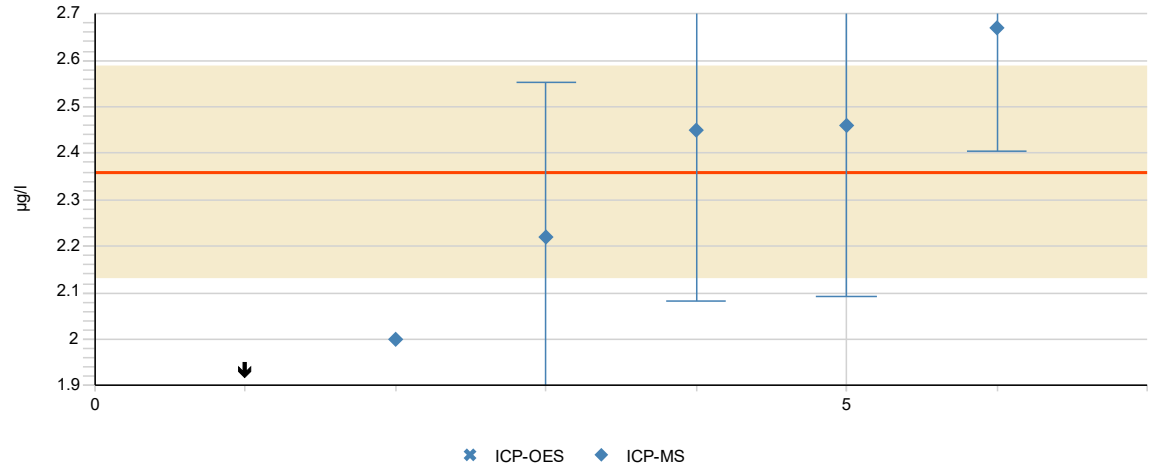

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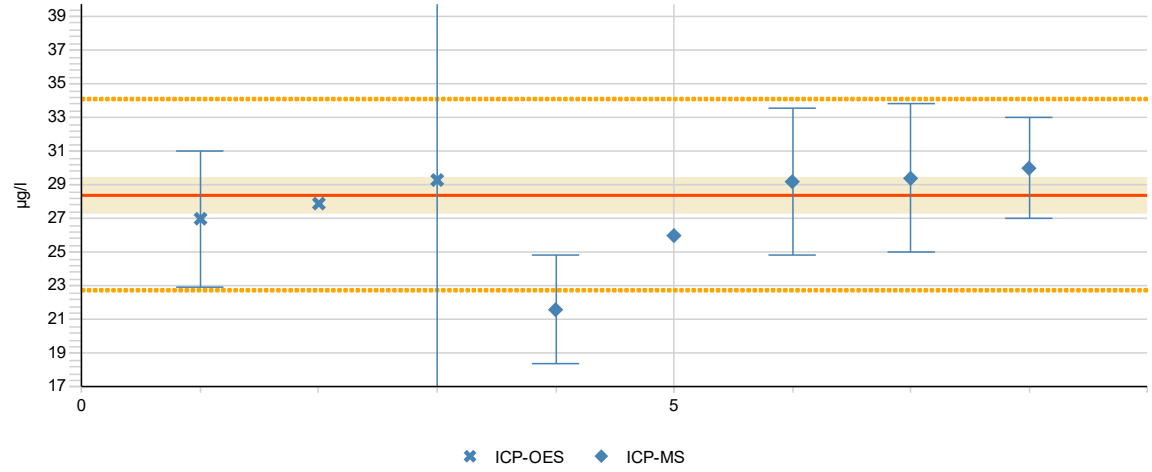
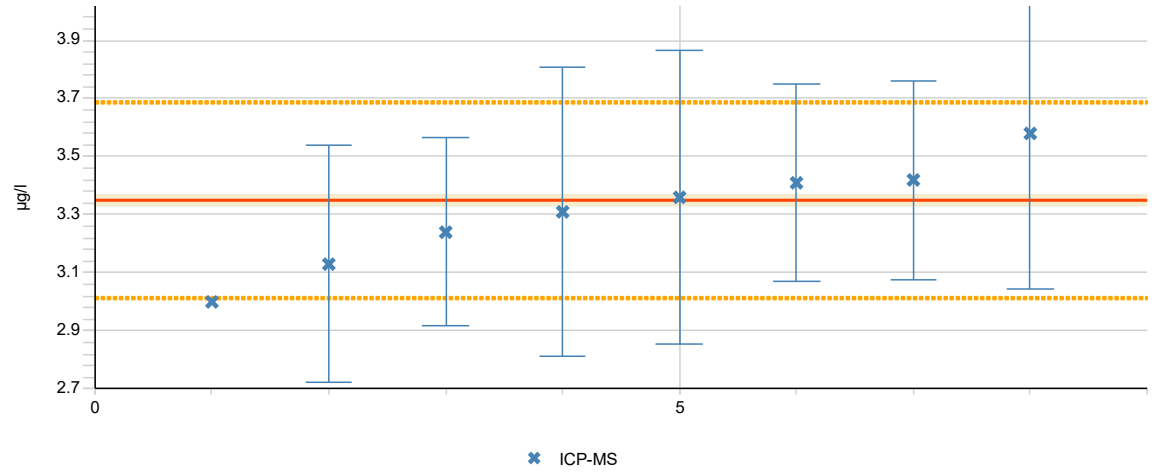
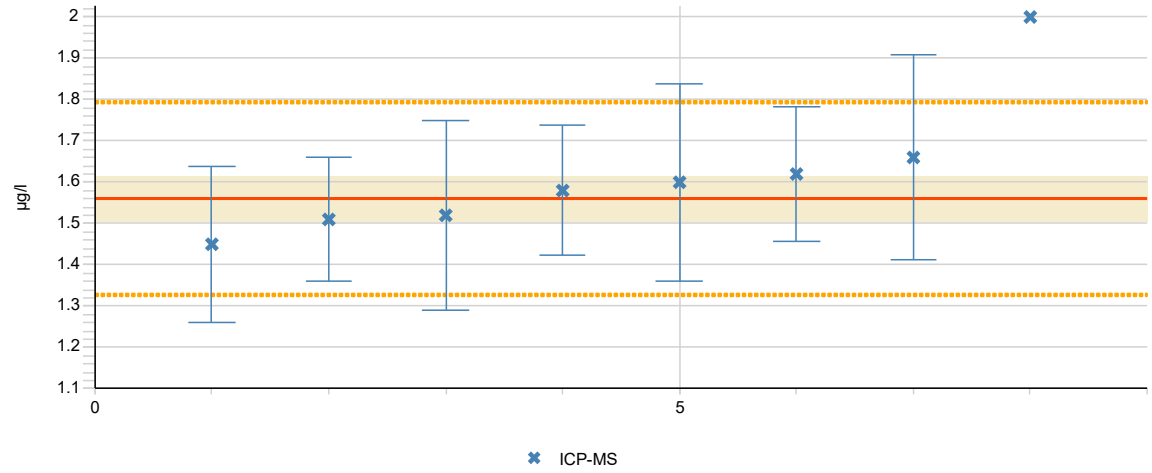


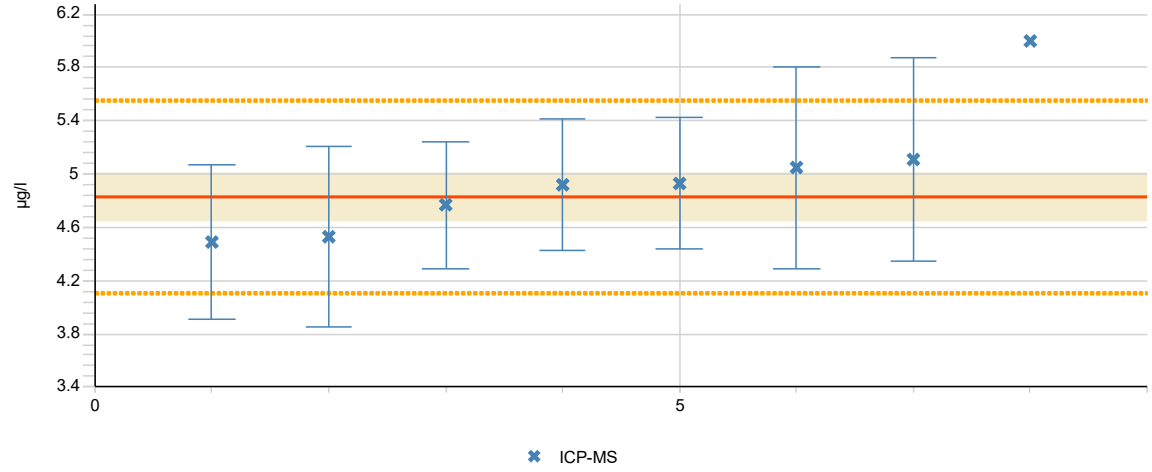
Measurand V Sample A1M



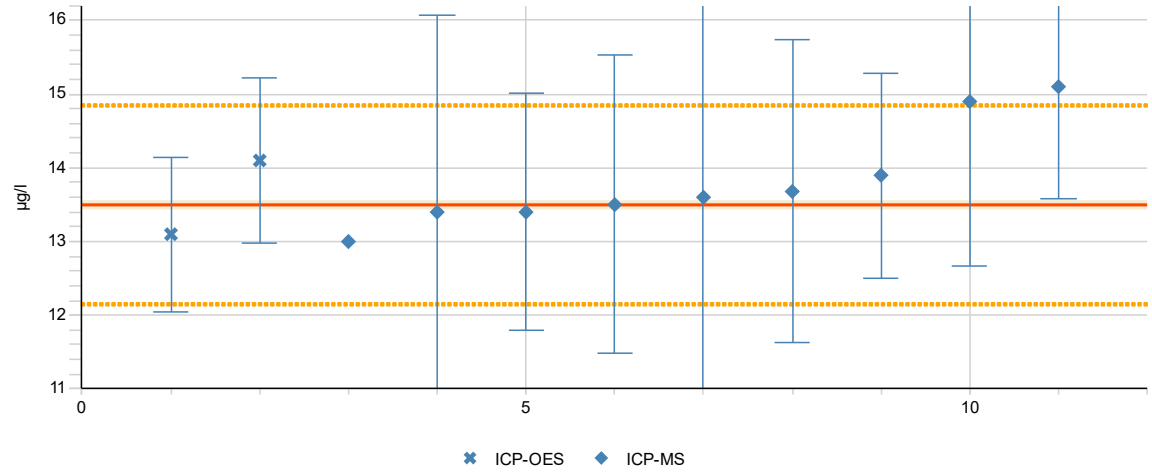
Measurand V Sample D2M



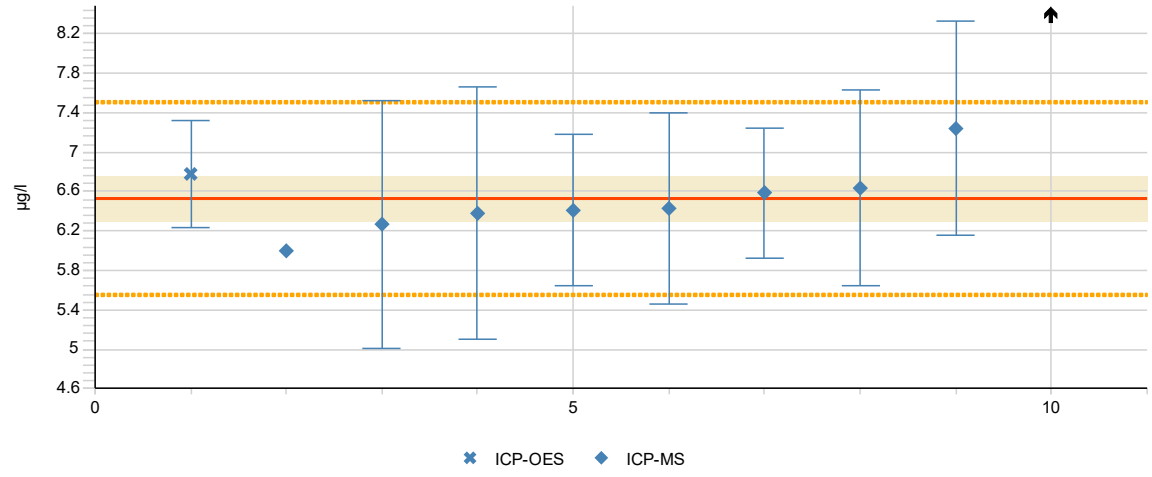
Measurand V Sample N3M

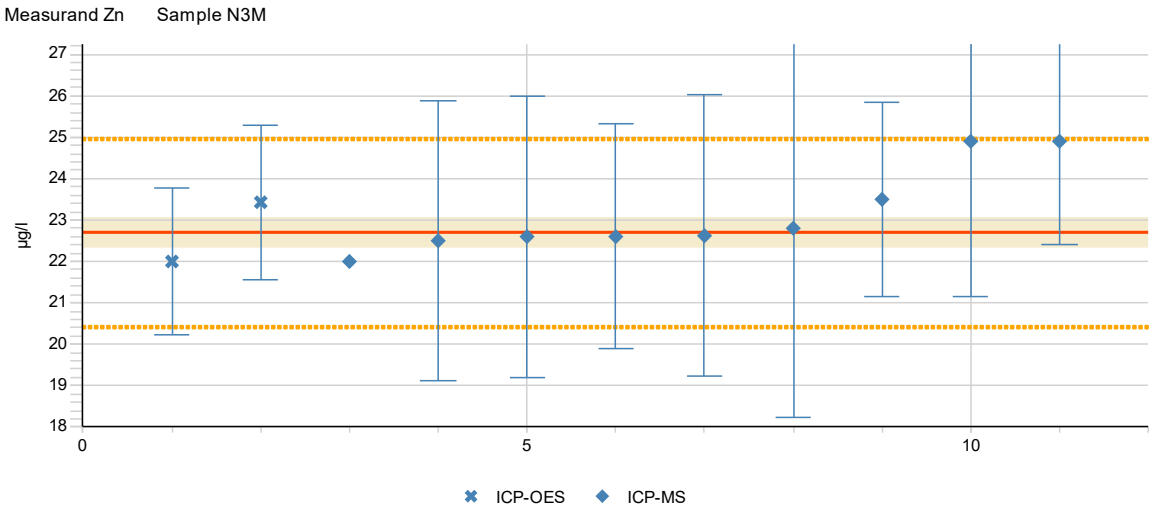


Measurand Zn Sample A1M



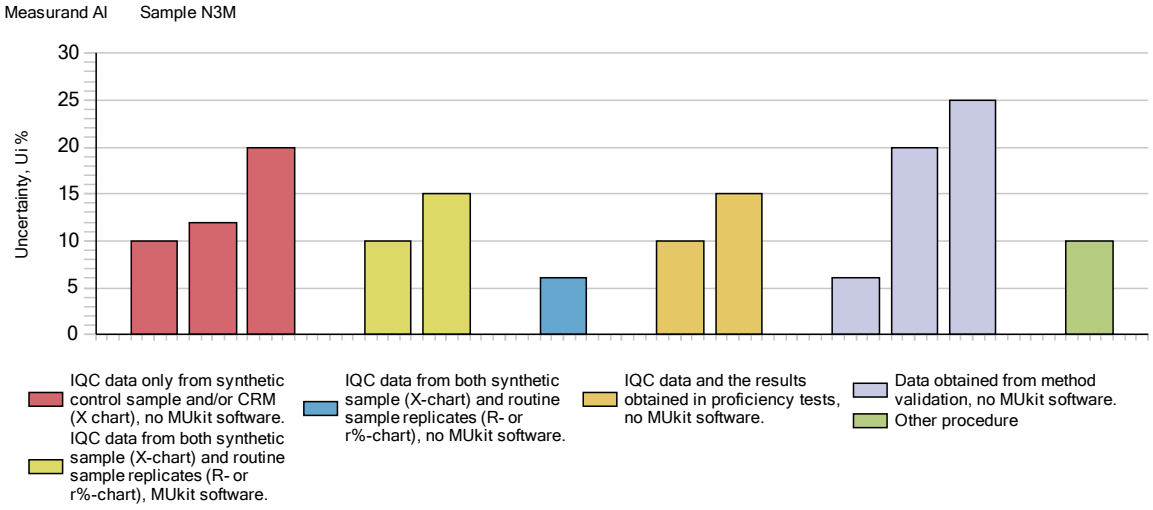
Measurand Zn Sample D2M

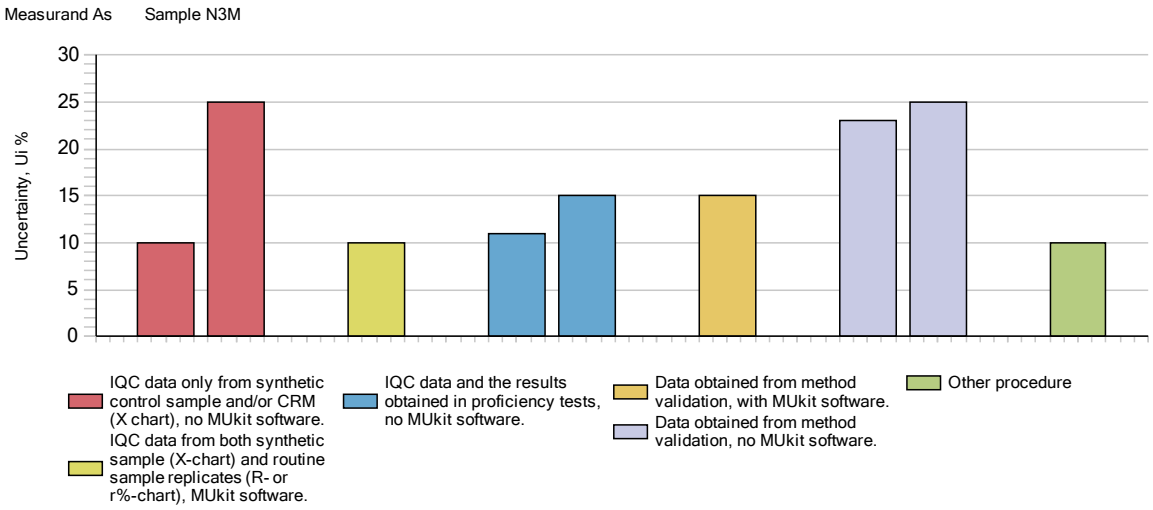



Measurand Zn
Sample N3M
µg/l
27
26
25
24
23
22
21
20
19
18
0
5
10
ICP-OES
ICP-MS

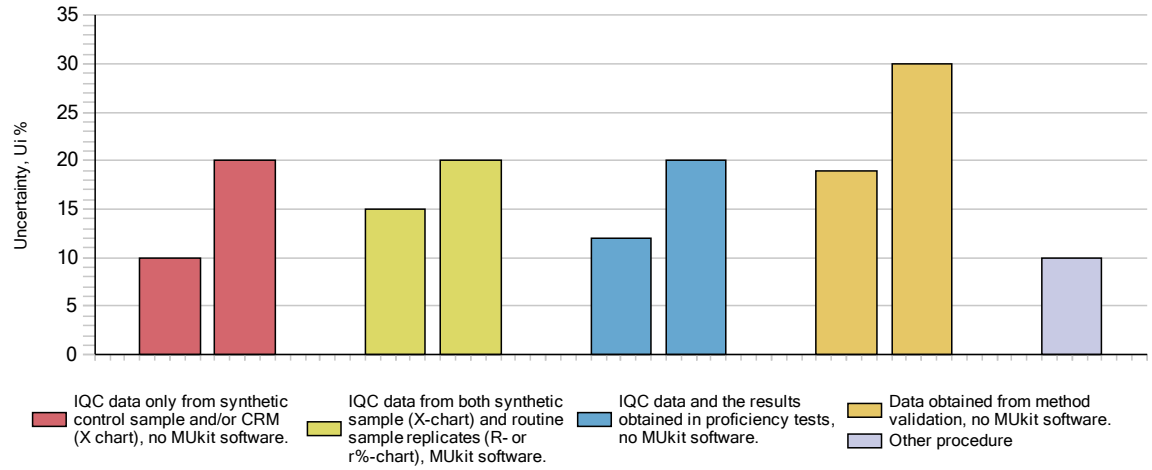
Appendix 11. Examples of measurement uncertainties reported by the participants

In figures, the presented expanded measurement uncertainties are grouped according to the method of estimation at 95 % confidence level (k=2). The expanded uncertainties were estimated mainly by using the internal quality control (IQC) data. The used procedures in figures below are distinguished e.g. between using or not using the MUkit software for uncertainty estimation [6, 7].

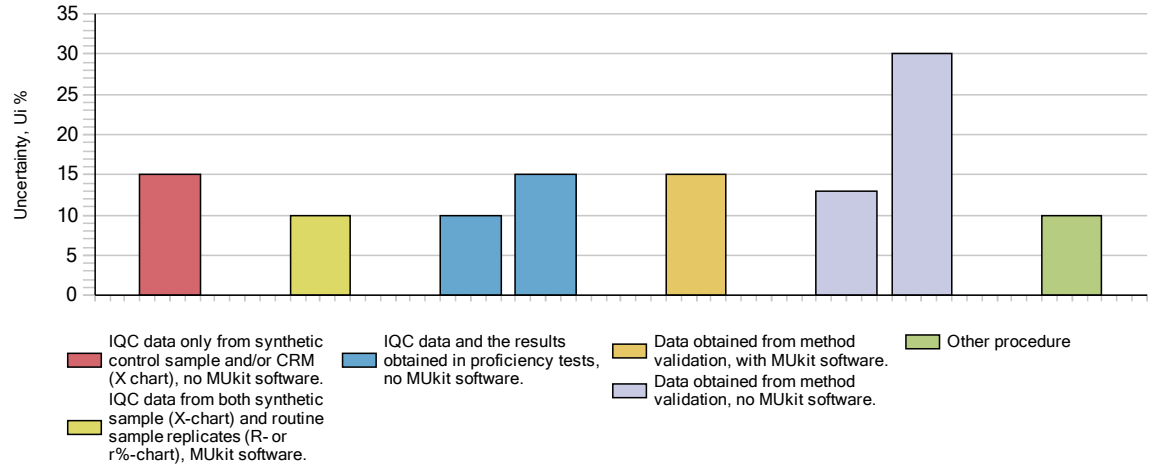




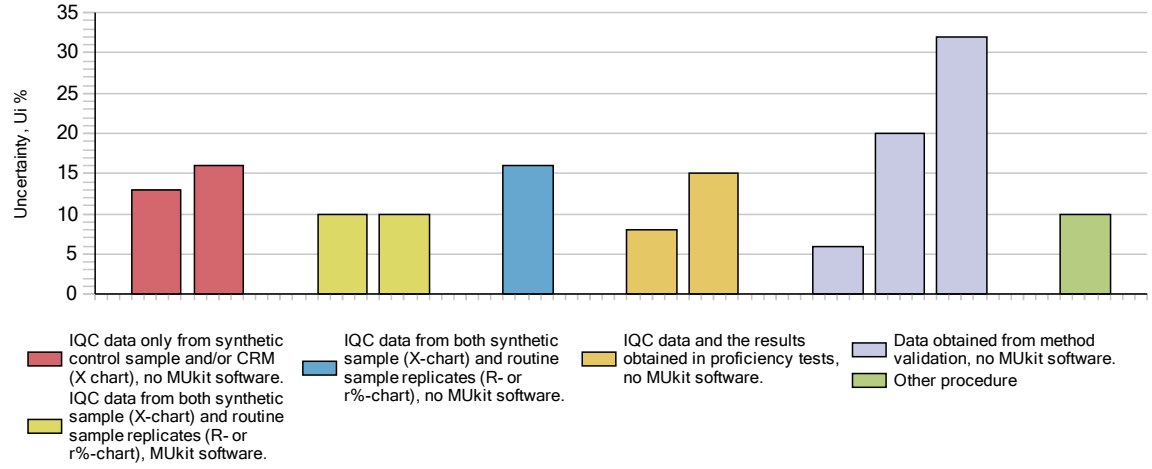
Measurand B Sample A1M



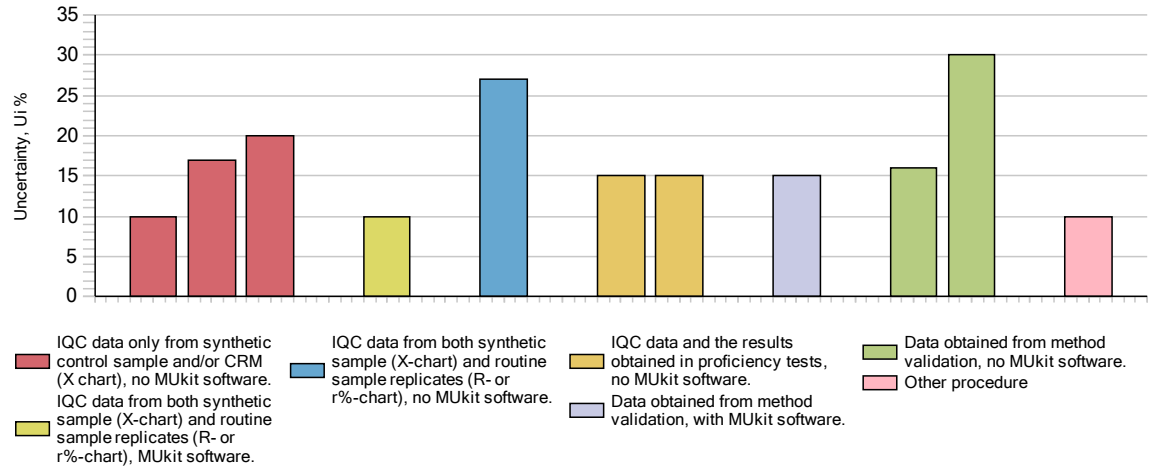
Measurand Ba Sample D2M



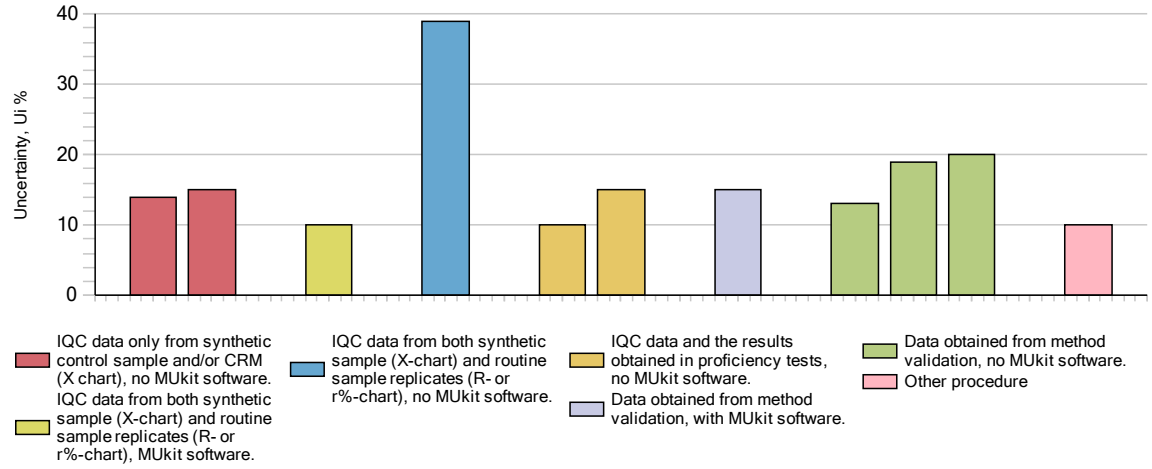
Measurand Ca Sample A1M



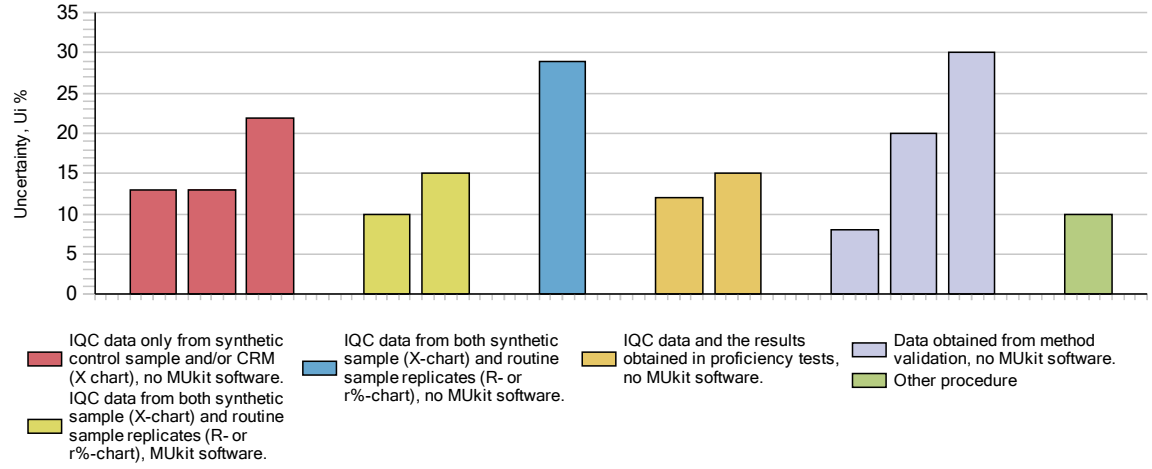
Measurand Cd Sample D2M



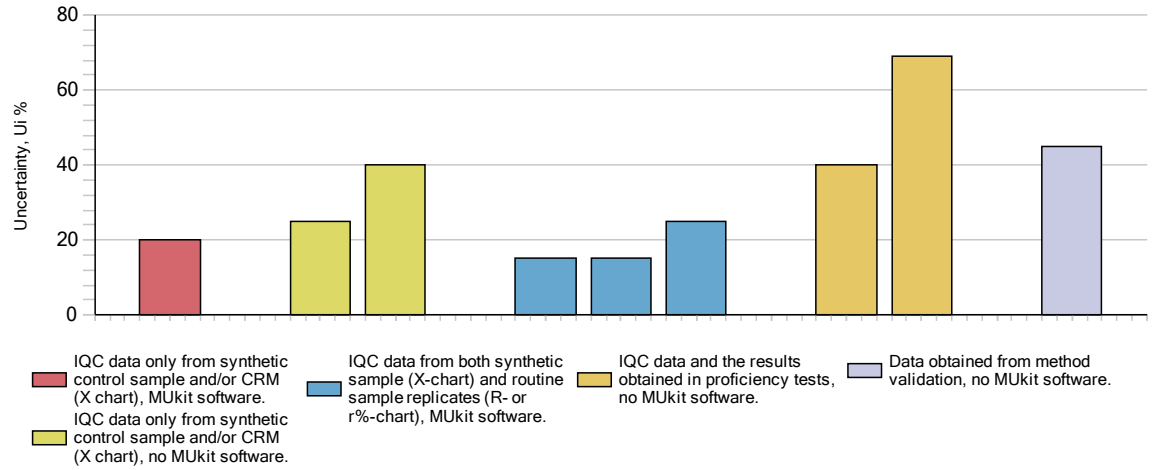
Measurand Cr Sample N3M



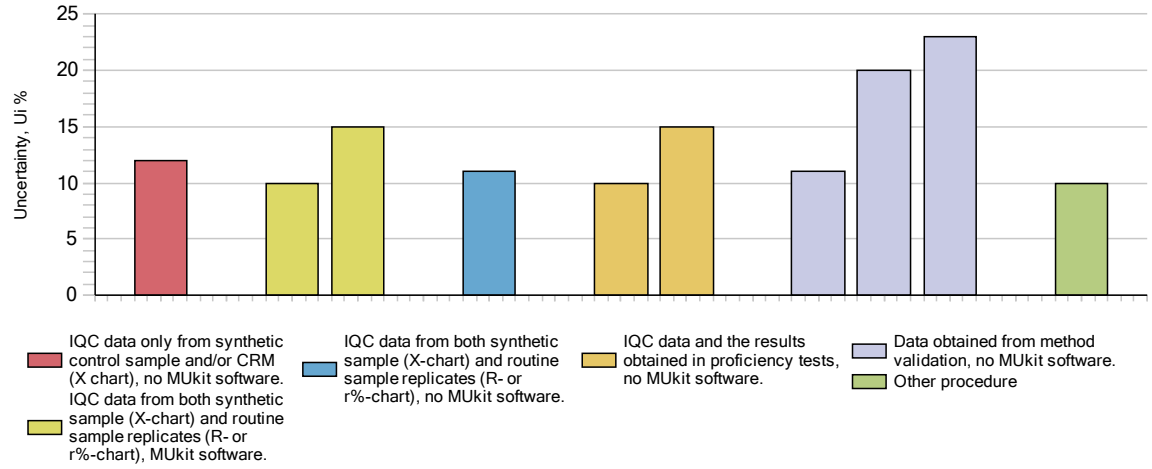
Measurand Fe Sample N3M



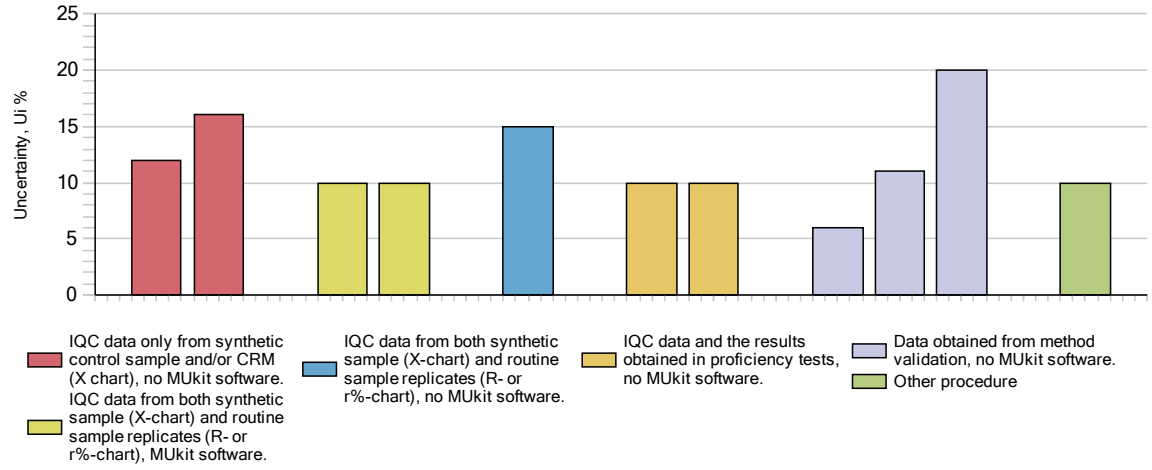
Measurand Hg Sample D2Hg



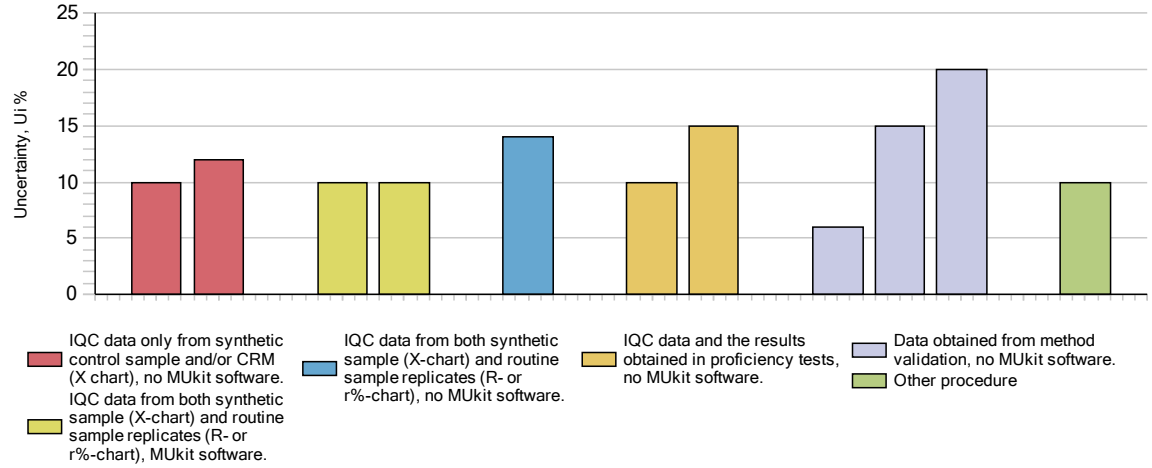
Measurand K Sample A1M



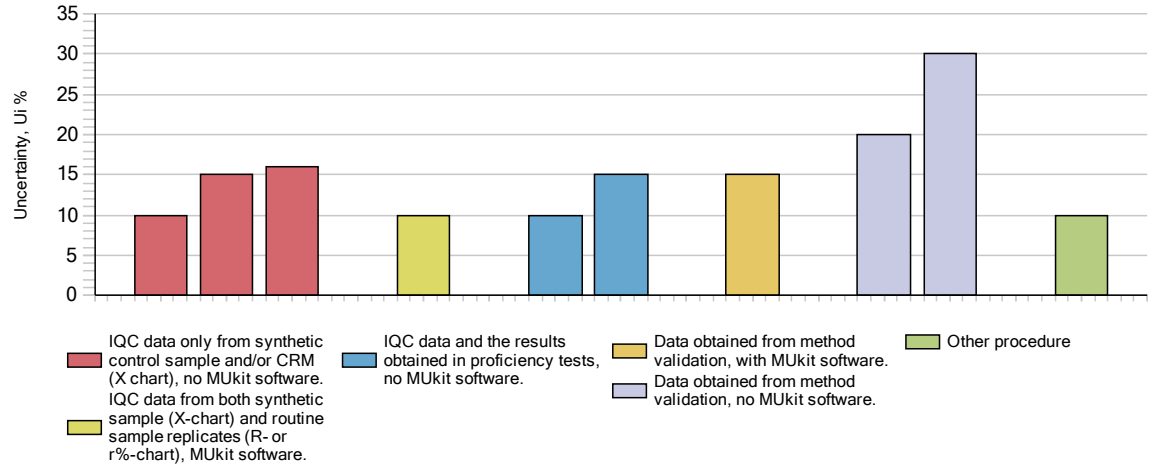
Measurand Mg Sample N3M



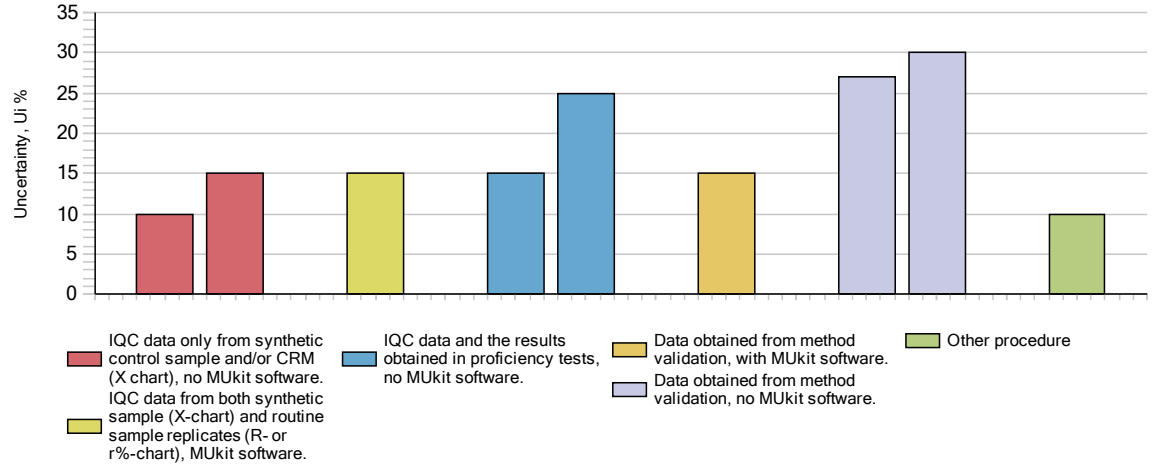
Measurand Na Sample N3M



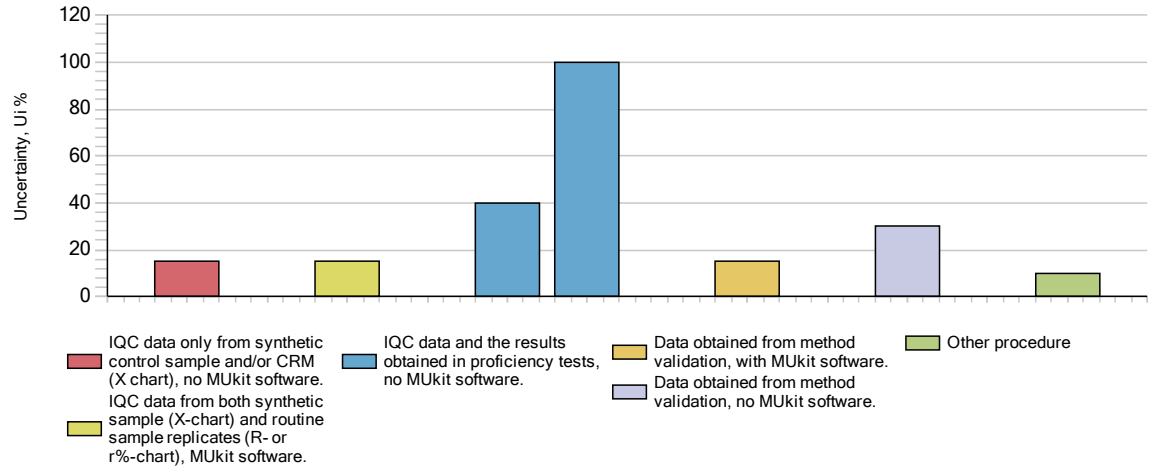
Measurand Pb Sample N3M



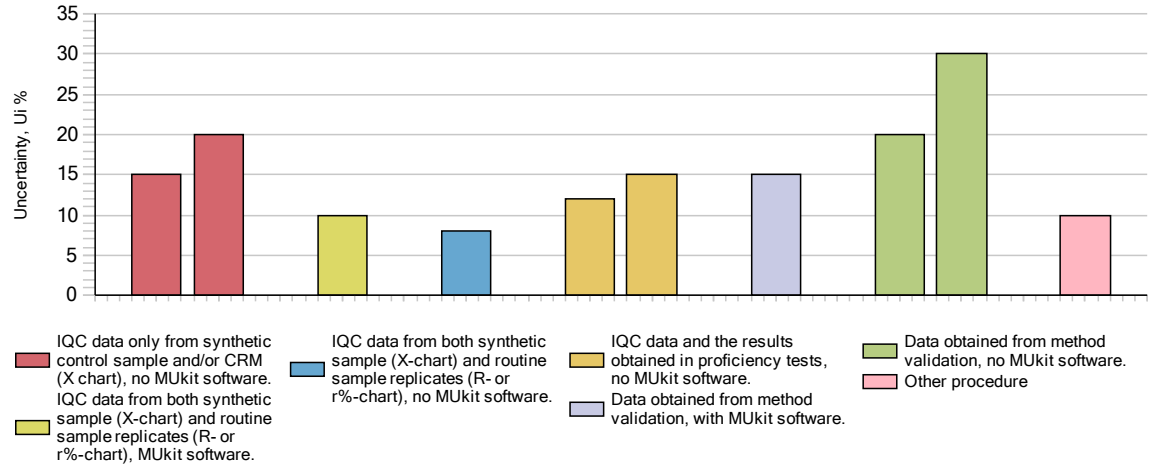
Measurand Se Sample D2M



Measurand Ti Sample D2M



Measurand Zn Sample D2M



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Finnish Environment Institute

ISBN 978-952-11-5426-3 (PDF)
ISSN 1796-1726 (online)